MATHEMATICAL MODELING OF LITHIUM BATTERY
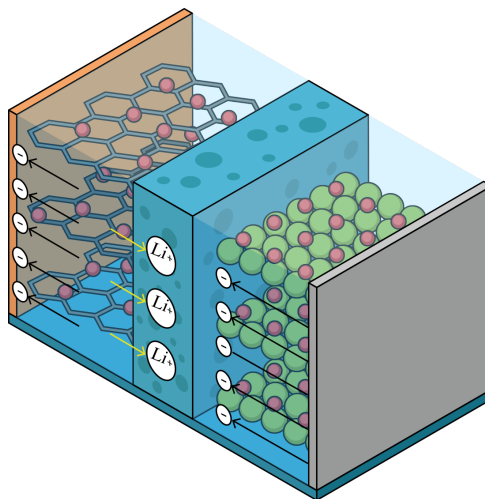

The transformation of chemical energy into electrical power using redox reactions is the fundamental process taking place in a battery. When the battery is rechargeable, this process can be reversed to store electrical energy in a chemical form. Li-ion batteries have the particularity of having very high energy density: A high amount of energy can be stored in a small volume. This property has been achieved by clever choices of materials. The discovery of such electrochemical cells is the result of fundamental research that was acknowledged by the Nobel prize in chemistry in 2019, see the Nobel prize webpage.

1. **Chemical reaction equilibrium**

The chemical potential enables us to measure the amount of energy that a chemical reaction can provide. Let us consider a system with a constituent that can take two forms X and Y,

$$X \longleftrightarrow Y.$$
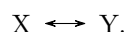
We denote by n_X and n_Y the number of X and Y, respectively. The Gibbs free energy, denoted G, is a function of pressure, temperature and composition (that is n_X and n_Y). The chemical potential of the species X is defined as the $\mu_X = \left(\frac{\partial G}{\partial n_X}\right)_{T,P,n_Y}$ and the corresponding expression for μ_Y. For a given temperature T and P, the equilibrium of a system is given by the state that minimizes the Gibbs free energy is minimum.

Question 1: ***Show that, for a given total number of constituents*** $n = n_X + n_Y$ ***and given pressure and temperature, the Gibbs free energy is minimum when the chemical potentials of X and Y are equal, that is***

$$(1) \qquad\qquad \mu_X = \mu_Y.$$

If $\mu_X > \mu_Y$, then we know that by transforming X into Y (at least in a infinitesimal way), we obtain a state with lower energy and the system will naturally evolve towards this state. **Kinetics**, which we will discuss later, consists of the study of the reaction rate, which determines how fast this evolution will take place. Let us consider the general reaction of the form,

$$\sum_{i=1}^{N} a_i X_i \longleftrightarrow 0,$$

where a_i can have a negative sign (for example $CH_4 + 2\,O_2 - CO_2 - 2\,H_2O \longleftrightarrow 0$). Let dn_{X_i} denote the (infinitesimal) change in the mole number of the chemical specie X_i.
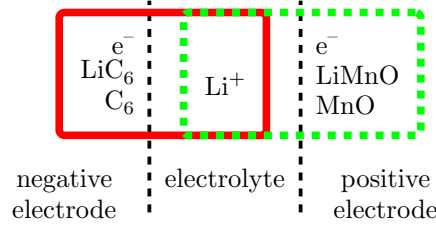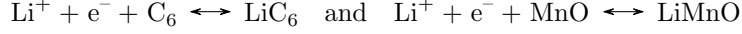
Question 2: **Show that we have the following constraint**

$$(2) \qquad \frac{1}{a_i} dn_{X_i} = \frac{1}{a_j} dn_{X_j},$$

for all pair i and j, at equilibrium or not. Taking into account the constraint (2), minimize the Gibbs free energy and show that at equilibrium we have

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

In a battery, we have two active materials at the electrodes which participate in the redox reactions. In the case of a lithium battery, standard choices are graphite (denoted C_6) at the negative electrode and transition metal oxides like Cobalt Oxide, Manganese Oxide (denoted MnO), Nickel Manganese Oxide or Iron Phosphate at the positive electrode. We write the redox reactions in the following simplified form,

$$\text{Li}^+ + \text{e}^- + \text{C}_6 \longleftrightarrow \text{LiC}_6 \quad \text{and} \quad \text{Li}^+ + \text{e}^- + \text{MnO} \longleftrightarrow \text{LiMnO}$$

negative electrode   electrolyte   positive electrode

We have two equilibria as depicted in the boxes above, which give us the same number of equations in term of the chemical potentials. At the negative electrode, we have

$$\mu_{\text{Li}^+}^{ne} + \mu_{\text{e}^-}^{ne} + \mu_{\text{C}_6}^{ne} = \mu_{\text{LiC}_6}^{ne}.$$

At the positive electrode, we have

$$\mu_{\text{Li}^+}^{pe} + \mu_{\text{e}^-}^{pe} + \mu_{\text{MnO}}^{pe} = \mu_{\text{LiMnO}}^{pe}.$$

We obtain the following difference of potential for the electrons between the negative and positive electrodes,

$$(4) \qquad \delta W = \mu_{\text{e}^-}^{ne} - \mu_{\text{e}^-}^{pe} = (\mu_{\text{LiC}_6}^{ne} - \mu_{\text{C}_6}^{ne}) - (\mu_{\text{LiMnO}}^{pe} - \mu_{\text{MnO}}^{pe}),$$

The difference δW has the dimension of an energy per mole and corresponds to the work that is needed to move a mole of electrons from the positive to the negative electrode. This quantity can be directly related to the **electrical potentials** ϕ^{pe} and ϕ^{ne} in Volt, at the positive and negative electrodes through the Faraday constant F,

$$(5) \qquad \delta W = F(\phi^{pe} - \phi^{ne}).$$

The Faraday constant is the electric charge of one mole of elementary carriers (e.g., protons). Here, we consider the case of an *open circuit*: The two electrodes are not connected with a conductor and since, by design, the electrolyte cannot contain free electrons, there is no current.

We have introduced two potentials, the chemical and electrical potentials. Potentials are a very important concept in thermodynamics. A potential is an intensive property and comes always in pair with an extensive property (see here for definitions). Her are the standard pairs

> (minus) pressure $\leftrightarrow$ volume
> temperature $\leftrightarrow$ energy (heat)
> chemical potential $\leftrightarrow$ number of the corresponding component (in mol)
> electrical potential $\leftrightarrow$ number of charges (in C)

Given two homogeneous closed systems which are not connected, we can measure the potentials in each system and compare them. When we open the two systems one for the other, a flux will be generated in the direction of **higher to the lower potential** values. For example, we can consider two boxes separated by an isolating fixed wall. The temperature are different on both sides. When we connect the two systems by letting the wall conduct heat, there is a transfer of energy from the higher to the lower temperature region.

Question 3: **What assumptions are made on the chemical potentials of the lithium ion Li^+ in the electrolyte to obtain (4) ? Give the open circuit voltage of a battery as a function of the chemical potential of its constituents.**

The chemical potentials, and therefore the open circuit voltage, depends on the concentrations of the different species in the electrodes and electrolyte. In Section 3, we will come back to that aspect. These concentrations will change as we operate the battery. Indeed, in a discharge scenario, the lithium will move from the negative to the positive electrode. This change in composition naturally induces a change in the circuit voltage. In particular, when the negative electrode gets empty, we get a very sharp decrease in the voltage.

2. Chemical reactions kinetics

Les us consider again a generic reaction of the form

$$X \longleftrightarrow Y.$$
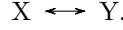
The reaction rate depends on the **concentrations**, the temperature and the value of the **activation energy**. Typically, in the reaction process, the elements (here in the form X) go through an unstable state of higher energy before reaching the new stable state where they take the form of the reaction product (here Y), see Figure 1, where we parameterize the reaction path using a scalar variable ξ. We represent the energy level per mole as a function of ξ. To reach the unstable equilibrium state, the element X needs an extra amount of energy, which corresponds to the activation energy E_a^f (here, the superscript f is an abbreviation for *forward* reaction). Then, it will release the energy E_a^b while reaching the new stable state where it takes the form Y (the superscript f stands here for *backward*). Using the Boltzmann
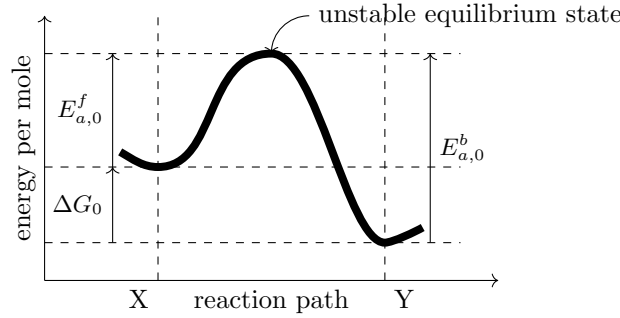

FIGURE 1. Reaction path and activation energy

distribution, we know that the probability that the element X reaches an energy larger or equal to E_a^f is proportional to $e^{-\frac{E_a^f}{RT}}$. Given a constant volume, we define the concentration of each species c_{X_i} as the number of moles per volume. The kinetic of the reaction, meaning here the rate of transformation of X in Y or vice-versa, is given by the law of mass action with a Arrhenius type of dependence on the activation energies,

$$(6) \qquad \frac{dc_Y}{dt} = -\frac{dc_X}{dt} = k \left(c_X e^{-\frac{E_a^f}{RT}} - c_Y e^{-\frac{E_a^b}{RT}} \right),$$

where c_X and c_Y are the concentrations of X and Y and k is a constant, independent of the other state variables (T, volume and the concentrations). For the general reaction of the form

$$(7) \qquad \sum_{i=1}^{N_X} a_i X_i \longleftrightarrow \sum_{i=1}^{N_Y} b_i Y_i,$$

this expression generalizes to

$$(8a) \qquad \frac{1}{b_i} \frac{dc_{Y_i}}{dt} = r, \qquad \frac{1}{a_i} \frac{dc_{X_i}}{dt} = -r$$

for all i, where the reaction rate r is given by

$$(8b) \qquad r = k_f e^{-\frac{E_a^f}{RT}} \prod_{i=1}^{N_X} c_{X_i}^{a_i} - k_b e^{-\frac{E_a^b}{RT}} \prod_{i=1}^{N_Y} c_{Y_i}^{b_i},$$

for some constants k_f and k_b.

Question 4: *Can you propose an interpretation of equation* (6) *and its generalization* (8) *based on a probability argument (probability that the elements meet and react)?*

We have derived earlier in (3) equilibrium conditions in terms of the chemical potentials of each species and of the stoichiometry (coefficients a_i that enters the chemical reaction (1)). The dependence in terms on the concentrations was not given and we propose now the expression

$$(9) \qquad \mu_{X_i} = \mu_{X_i}^0 + RT \ln\left(\frac{c_{X_i}}{c_0}\right).$$

In (9), c_0 is a reference concentration, typically set to $1\,\text{mol}\,\text{L}^{-1}$. The value of $\mu_{X_i}^0$ is the *standard* potential, that is the potential obtained at the reference concentration. In general μ_{X_i} depends on *all* the concentrations (and not only c_{X_i}). The expression (9) corresponds to the special case of a *dilute* solution, where we neglect any form of interaction between the different species.

The kinetic equations given in (8) yield by themselves equilibrium equations. Let us check that the two expressions of the equilibrium equations we have introduced independently are consistent.

Question 5: *What are the equilibrium equations we obtain from* (8)*? Show that they are consistent with the expressions given by* (3) *and* (9) *and write down the compatibility conditions between the parameters involved in both formulations.*

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

Let us now consider reactions that involved charged species. We consider the redox reaction

$$(10) \qquad \text{Li} \longleftrightarrow \text{Li}^+ + \text{e}^-.$$

3.1. **Equilibrium equations.** Let us first consider the case where the reaction (10) is at equilibrium. In the presence of an electrical field, the energy of the *charged* species will change. Positively charged species become more energetic when the electrical potential increases and the reverse is true for negatively charged species. We introduce the **electro-chemical** potential $\tilde{\mu}_X$ as the sum of the chemical potential and the electrical potential U potential,

$$(11) \qquad \tilde{\mu}_X = \mu_X + zFU.$$

Here z denotes the charge number of X and F is the Faraday constant (the charge number of Li^+ is $z_{\text{Li}^+} = 1$). For Li and Li^+, we use the chemical potential given by (9). The electro-chemical potential of the electron in the electrode is directly related to the electrical potential through the expression

$$(12) \qquad \tilde{\mu}_{\text{e}^-} = -FU.$$

We have a minus sign because the electron is negatively charged. When the battery is open, the electrons cannot move. An equilibrium is reached though the creation of a potential drop between the electrode and electrolyte. The equilibrium equation (3) holds but now for the *electro-chemical* potentials. In the electrolyte, close to the electrode, there exists a thin interface layer, the double layer, where the electrical potential changes very rapidly. We consider two values of the electrical potential U: The value U_{elde} at the electrode, which applies to the electron in the solid electrode and the value U_{elyte} in the electrolyte beyond the interface layer. The electrical potential U_{elyte} applies to the lithium ion Li^+. We set $U_{\text{eq}} = U_{\text{elde}} - U_{\text{elyte}}$.

Question 6: *Give the expression of the open circuit potential U_{eq} as a function of the concentrations c_{Li} and c_{Li^+}.*

3.2. **Kinetics equations.** In Figure 1, we presented the energy variation across the reaction path without considering the fact that we may have charged particle. When we apply a electrical potential at the electrode, the reaction path is changed. The electrical potential will only change the electrochemical potential of the charged particles. In general, when we increase the electrical potential, the electrochemical potential of the lithium ion would increase while the electrochemical potential of the electron decreases. However, there exists a shielding effect for the lithium ion which results in that its electrochemical potential is not affected by the change in the electrode potential. The only remaining effect is then the decrease of the electrochemical potential of the electron. The situation is illustrated in Figure 2.

We relate the change in the activation energies to the change of electrical potential as follows

$$F\delta U = \underbrace{(E_{a,0}^f - E_{a,0}^b)}_{\Delta G_0} - \underbrace{(E_a^f - E_a^b)}_{\Delta G},$$
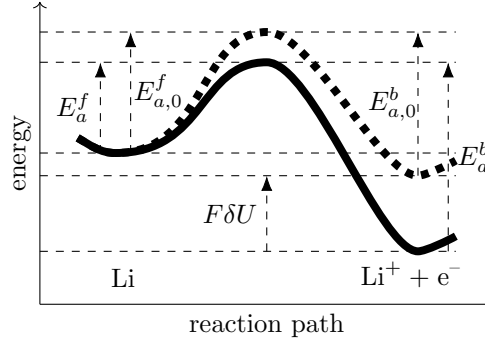
FIGURE 2. Reaction path and activation energy at some reference potential (dashed line and activation energies given by $E_{a,0}^f$ and $E_{a,0}^b$) and after increasing the electrical potential with δU (plain line and activation energies given by E_a^f and E_a^b). In this figure, we have $\delta U > 0$ and we see that the energy of the complex $\text{Li}^+ + \text{e}^-$ decreases.

see Figure 2. The variation in electrical potential is split into two: a contribution to the the change of the forward activation energy and another to the change of the backward activation energies. We write

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

for some $\beta \in [0,1]$. The constant β depends on the materials. The default choice is to assume an equal distribution, that is $\beta = \frac{1}{2}$.

Let us use the kinetic equation (6) with X = Li and Y = Li^+, meaning that we consider the chemical reaction Li $\longleftrightarrow$ Li^+ and assume that the influence of the electron is fully captured by the change in the activation energy (In particular, we do not consider the electron concentration. Note that the kinetic equations (6) there hold for dilute solutions).

Question 7: **Derive a function of the potential difference as a function of the concentration which holds at equilibrium and which is of the form**

(13)
$$U_{eq} = \frac{RT}{F} \ln\left(\frac{c_{Li^+}}{c_{Li}}\right) + \frac{\Delta G_0}{F}.$$

An expression for the equilibrium potential U_{eq} was obtained in Question 6.

Question 8: **Show that the expressions for U_{eq} given by (13) and obtained in Question 6 are consistent. What are the compatibility conditions for the parameters involved in both expressions?**

Let us denote by ϕ_{elde} and ϕ_{elyte} the electric potential in the electrode and the electrolyte. We consider now the case where there is a *current* between the two components. We denote the intensity of the current by i and it corresponds to the amount of positive charge created per time (unit is Ampere). The value of

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

denotes the **surface over-potential**. If $\eta = 0$, there is no charge transfer. It $\eta > 0$, then a current will be created in the direction of the electrode to the electrolyte. If $\eta < 0$, a current will be created in the opposite direction. Note that, by current, we mean a flux of *positive* charges. The *flux* of charges comes from the chemical reaction. A creation of Li^+ corresponds to an incident current in the electrolyte.

Question 9: **Derive the following relation between the volumetric current (defined below) and the surface over-potential**

(14)
$$i = i_0 \left(e^{-\left(\frac{(1-\beta)F\eta}{RT}\right)} - e^{\left(\frac{\beta F \eta}{RT}\right)} \right),$$

where $\eta = \phi_{elde} - \phi_{elyte} - U_{eq}$ and

(15)
$$i_0 = Fk \left(c_{Li} e^{-\frac{E_{a,0}^f}{RT}} \right)^{1-\beta} \left(c_{Li^+} e^{-\frac{E_{a,0}^b}{RT}} \right)^{\beta}.$$

Here, we define the *volumetric current* i as $i = -F\frac{dc_{e^-}}{dt}$ where $c_{\text{e-}}$ is the number of electrons per volume (in $\text{mol}\,\text{m}^{-3}$).

Equation (14) is called the Butler-Volmer equation and is ubiquitous in electro-chemistry.

4. Charge conservation equation

Let ρ be a charge density $(\mathrm{C\,m^{-3}})$ and j denote the current density. The current density is the flow of electric charge per unit of surface $(\mathrm{A\,m^{-2}})$

Question 10: ***Derive the charge conservation equation***

$$\frac{\partial \rho}{\partial t} + \nabla \cdot j = 0. \tag{16}$$

We assume charge neutrality, that is ρ is constant and equal to zero. We consider a cylindric wire of length L with given imposed uniform electrical potential ϕ_L and ϕ_R at the extremities and no flux at the sides, see Figure 3. We assume that the current density follows the Ohm law given by $j = \sigma E$, where σ is the conductivity in Siemens per meter $(\mathrm{S\,m^{-1}})$, E is the electrical field and E derives from an electrical potential through the expression $E = -\nabla \phi$.

Question 11: ***Solve equation*** (16) ***for this setup (charge neutrality assumption, geometry, boundary conditions) and establish that***

$$U = RI,$$

for $U = \phi_L - \phi_R$***,*** $I = -\int_{S_L} j \cdot n \, dS = \int_{S_R} j \cdot n \, dS$ ***and*** $R = \frac{L}{\sigma A}$***.***
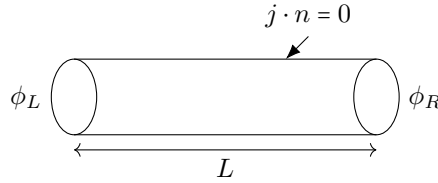
Here, A is the area of the wire.

FIGURE 3. Illustration of a cylindrical wire with the applied boundary conditions.

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 will now consider only the activation phase, that is when t remains very small. Thus, we assume that no ions have had time to significantly move in the electrolyte or lithium to diffuse in the electrode. We assume also that the lithium distribution in the electrolyte and the electrode is homogeneous (the ion concentrations are constant in space). To simplify expression (14), we consider $\beta = \frac{1}{2}$. Let us then use an expression that has the same form as (14) but for a current in Ampere, meaning that, for each electrode, we use an expression of the form

$$I = I_0 \sinh\left(\frac{F\eta}{2RT}\right),$$

for I_0 given. The assumptions above imply that I_0 is assumed to be constant in the short interval of time we are considering. We assume a constant resistance in all the components (electrodes and electrolyte), which we denote R_{ne}, R_{pe} and R_{elyte}. We assume also that the potential at the negative electrode is kept constant. In Figure 4, we plot the potential in the different regions at equilibrium when $t < 0$ and illustrates also how it will look like for $t \geq 0$.

Question 12: ***Find a relation between the potential drop*** $U = \phi_+ - \phi_-$ ***and the current*** I ***of the form*** $U = f(I)$***.***

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
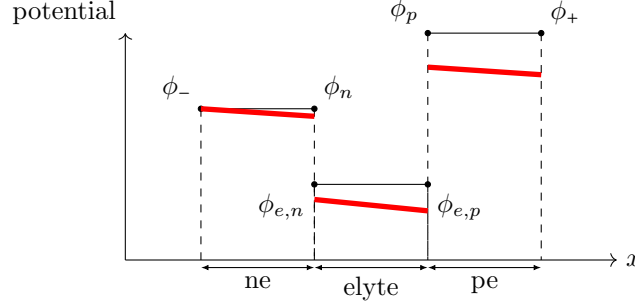
FIGURE 4. Illustration of the activation phase. We plot two configurations : $t < 0$ (black, no current) and $t \geq 0$ (red, current equal to $I > 0$). The current inside the battery is going from left to right from states of lower to higher electrical potential. This can be only be achieved by an energy contribution from the chemical reactions in the battery. Note the decrease of the net difference $\phi_+ - \phi_-$ when the battery gets activated.

microscopic forces. For a given ion indexed by i, we denote by N_i the flux in $\mathrm{mol\,m^{-2}\,s^{-1}}$. The flux is given by

$$(17) \qquad N_i = -z_i u_i F c_i \nabla \phi - D_i \nabla c_i$$

where, for the ion i, z_i is the charge number , u_i is the **mobility** (in $\mathrm{m^2\,mol\,J^{-1}\,s^{-1}}$), c_i is the concentration, D_i is 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 $(\mathrm{A\,m^{-2}})$ in a electrolyte is indeed given by the sum of the ion fluxes multiplied with the Faraday constant,

$$(18) \qquad j = F \sum_{i=1}^{N} z_i N_i.$$

To understand the migration term $-z_i u_i F c_i \nabla \phi$ in (17), let us use classical electrodynamics. The force on a charged particle (with charge q in Coulomb) is $f = qE = -q\nabla\phi$. In the only presence of the electrical field, Newton's law used alone would imply that the particle velocity grows at a constant rate towards infinity (we assume E constant). However, in an electrolyte, the charged ions cannot freely accelerate as they collide with other molecules (charged and neutral). Let us model this effect as a friction force, $f_{\mathrm{friction}} = -|q|\tau_i v$ where v is the velocity and τ some constant friction coefficient.

Question 13: *Relate the coefficient τ_i with the mobility u_i. Compute the conductivity of the electrolyte when we neglect the diffusion term.*

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 $\mathrm{Li^+}$ and hexafluorophosphate ion $\mathrm{PF_6^-}$. The governing equations are given by

$$(19a) \qquad \frac{\partial c_+}{\partial t} = u_+ F \nabla \cdot (c_+ \nabla \phi) + D_+ \Delta c_+,$$

$$(19b) \qquad \frac{\partial c_-}{\partial t} = -u_- F \nabla \cdot (c_- \nabla \phi) + D_- \Delta c_-$$

and

$$(19c) \qquad c_+ - c_- = 0.$$

The later equation expresses electrical neutrality.

Question 14: *Explain how the governing equations* (19) *are derived. Explain how* (19c) *follows from the charge conservation equation, $\nabla \cdot j = 0$, and* (19a) *and* (19b)*.*

7. Modeling equations for the whole battery

We consider a 2D battery with two electrodes and an electrolyte. At the external side of the positive electrode, we impose a constant current 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 in its different form ($\mathrm{LiC_6}$, $\mathrm{Li^+}$ and LiMnO), see Figure 5 and the notations within. The governing equations in the electrolyte are given by (19), which correspond to mass and charge conservation. In the electrodes,

the lithium components (LiC_6 and $LiMnO$) are also described by their concentrations, denoted c_{ne} and c_{pe}, and their motion is governed by a diffusion process. In these three domains, the governing equations are given by mass conservation and charge conservation.
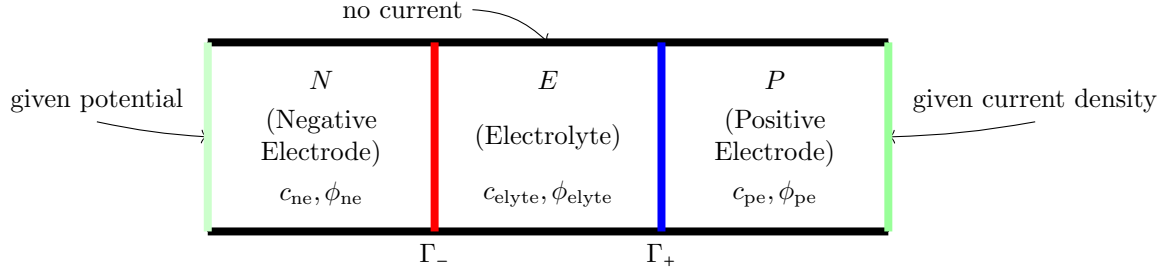

FIGURE 5. Battery model

Question 15: *Consider a 3D model and write down the governing equations for each of the domain (P, N and E). Include the boundary conditions and in particular the interface conditions at Γ_+ and Γ_- where the chemical reactions occur.*

Let us now consider the one-dimensional case. Then, the geometry is the same as in Question 12. Let us denote the solution found there in each domain with the superscript zero and use it as initial solution. We want to derive the equations for the short time solution, that is $t = \varepsilon\bar{t}$ for $\varepsilon \ll 1$ and $\bar{t} \approx 1$. We use an asymptotic assumption

$$(20) \qquad c_\alpha(\bar{t}, x) = c_\alpha^0(x) + \varepsilon c_\alpha^1(\bar{t}, x), \quad \phi_\alpha(\bar{t}, x) = \phi_\alpha^0(x) + \varepsilon\phi_\alpha^1(\bar{t}, x)$$

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

Question 16: *Use the expansions above to obtain a linear approximation of the governing equations. Try to solve those numerically.*

Symbol	Description	Unit
G	Gibbs free energy	J
μ_X	Chemical potential of component X	$J\,mol^{-1}$
ϕ	Electrical potential	V
N_i	Molar flux of component i	$mol\,s^{-1}\,m^{-2}$
F	Faraday constant	$C\,mol^{-1}$
E_a	Activation energy	$J\,mol^{-1}$
z	Charge number	no unit
D	Diffusion coefficient	m^2/s
c	Concentration	$mol\,m^{-3}$
u	Mobility	$m^2\,mol\,J^{-1}\,s^{-1}$
j	Current density	$A\,m^{-2}$
I	Current	A
ρ	Charge density	$C\,m^{-3}$
σ	Conductivity	$S\,m^{-1}$
R	Ideal gas constant	$J\,K^{-1}\,mol^{-1}$

TABLE 1. Symbol with definition and unit