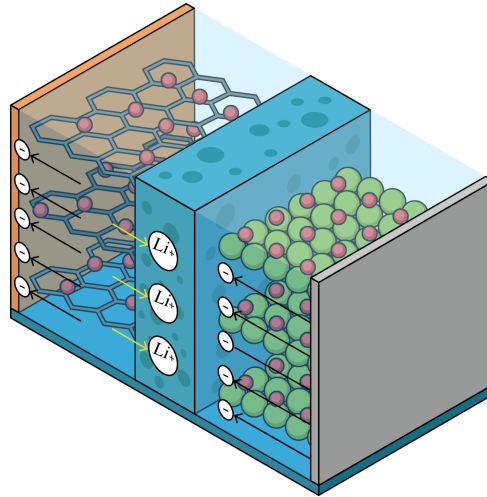


TMA4195 - FALL 2021
 MATHEMATICAL MODELING OF LITHIUM BATTERY

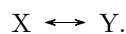


The transformation of chemical energy into electrical power using redox reactions is the fundamental process taking place in a battery. When the battery is rechargeable, this process can be reversed to store electrical energy in a chemical form. Li-ion batteries have the particularity of having very 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](#).

The goal of this project is to set up the mathematical models that can capture some of the essential processes taking place in a battery. When possible, we will use those models to write simulation code able to predict some properties of the battery.

1. Chemical equilibrium and Gibbs free energy

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,

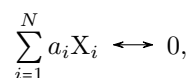


We denote by n_X and n_Y the number of X and Y, respectively. The Gibbs energy is a function of pressure, temperature and composition (that is n_X and n_Y). The chemical potential of X is defined as the $\mu_X = \left(\frac{\partial G}{\partial n_X}\right)_{T,P,n_Y}$ and the corresponding expression 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*

$$\mu_X = \mu_Y.$$

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 evolves towards this state - if possible. Kinetics, which we will discuss later, addresses then the aspect of how fast this evolution will take place. Let us consider the general reaction of the form,



where a_i can have a negative sign (for example $C + O_2 - CO_2 \leftrightarrow 0$). Let dn_{X_i} denote the (infinitesimal) change in the mole number of the chemical specie X_i .

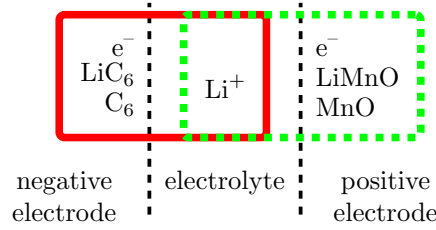
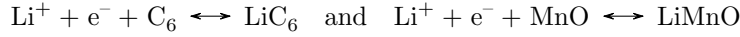
Question 2: *Show that we must have*

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

for all pair i and j . Show that a condition for equilibrium (i.e. the minimization of the Gibbs energy) is

$$(2) \quad \sum_{i=1}^N a_i \mu_{X_i} = 0.$$

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



We have two equilibrium 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

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

At the positive electrode, we have

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

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

$$(3) \quad \delta W = \mu_{\text{e}^-}^{ne} - \mu_{\text{e}^-}^{pe} = (\mu_{\text{LiC}_6}^{ne} - \mu_{\text{C}_6}^{ne}) - (\mu_{\text{LiMnO}}^{pe} - \mu_{\text{MnO}}^{pe}),$$

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 ,

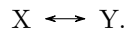
$$(4) \quad \delta W = F(\Phi^{pe} - \Phi^{ne}).$$

The Faraday constant is the (absolute) charge of one mole of electrons.

Question 3: *Explain how (4) derives from (3) and give the “voltage” of a battery as a function of the chemical potential of its constituents.*

2. Kinetics of chemical reactions in solutions

Let us consider again a generic reaction of the form



Even if the reaction from X to Y is exothermic (the energy of a mole of X is higher than the one of a mole of Y), not all the elements X are going to be transformed instantaneously in Y. The reaction rate depends on the concentrations, temperature and value of the **activation energy**. Typically, in the reaction process, the elements (here in the form X) go through an instable 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 and represent the energy level of element 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*). The total energy release is equal to $\Delta G = E_a^b - E_a^f$. Using the [Boltzmann distribution](#), we can infer that the probability that the element

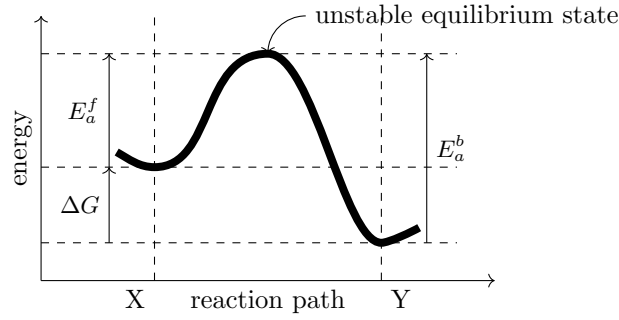
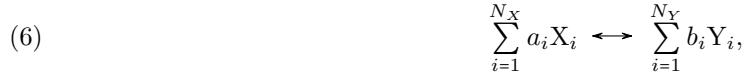


FIGURE 1. Reaction path and activation energy

X reaches a 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 and vice-versa, is given by

$$(5) \quad \frac{dc_Y}{dt} = -\frac{dc_X}{dt} = k_f c_X e^{-\frac{E_a^f}{RT}} - k_b c_Y e^{-\frac{E_a^b}{RT}},$$

where c_X and c_Y are the concentrations of X and Y and k_f and k_b are some constants, independent of the other state variables (T , volume and the concentrations). For the general reaction of the form



this expression generalizes to

$$(7) \quad \frac{1}{b_i} \frac{dc_{Y_i}}{dt} = r, \quad \frac{1}{a_i} \frac{dc_{X_i}}{dt} = -r$$

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

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

for some constant k_f and k_b .

Question 4: *Can you propose an interpretation on equation (5) and its generalization (7) based on a probability argument (probability that the elements meet and react)? What are the equilibrium equations? (note that they do not depend on the activation energy but only on ΔG).*

3. Effect of the electrical state of the reaction kinetics

We consider a redox reaction



where O denotes the oxidized species and R denotes the reduced species. When we change the electrical state, by changing the external electrical potential from some reference potential U_0 to U , we change the reaction function path, as depicted in Figure 2. We relate the change in the reaction Gibbs energies per mole to the change of electrical potential, again using the Faraday constant,

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

The variation in electrical potential is split in two contributions in the change of the forward and backward activation energies,

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

for some $\beta \in [0, 1]$.

Question 5: *Use the kinetic equation (5) and derive a function of the potential difference as a function of the concentration which holds at equilibrium and which is of the form*

$$(10) \quad \delta U_{eq} = -\frac{\Delta G_0}{F} + \frac{RT}{F} \ln\left(\frac{c_O}{c_R}\right) + \frac{RT}{F} \ln\left(\frac{k_b}{k_f}\right)$$

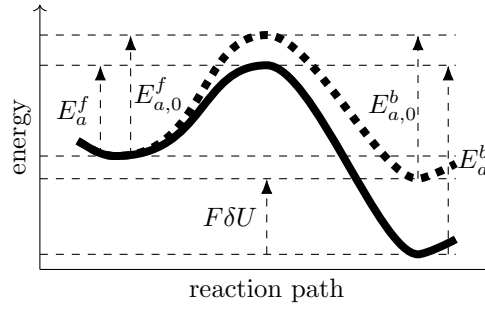


FIGURE 2. Reaction path and activation energy at some reference potential (dashed line) and after increasing the electrical potential with δU (plain line). In this figure, we have $\delta U > 0$, as we can see that the energy of the electron get decreased.

Relation (10) will give us how the electrical potential at an electrode-electrolyte interfaces depends on the concentration of the redox species.

Let us consider an electrode - electrolyte system (say LiC_6 and Li^+) and we 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 them. 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

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

is called the surface overpotential and denoted η and represents the deviation from the equilibrium potential. If $\eta = 0$, there is no charge transfer and otherwise, an electrical current is going to be created as the result of the electro-chemical reaction.

Question 6: *Derive the following relation between the current and the surface overpotential*

$$(11) \quad i = i_0 \left(e^{-\left(\frac{(1-\beta)F\eta}{RT}\right)} - e^{\left(\frac{\beta F\eta}{RT}\right)} \right),$$

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

$$(12) \quad i_0 = F \left(k_f c_R e^{-\frac{E_{a,0}^f}{RT}} \right)^{1-\beta} \left(k_b c_O e^{-\frac{E_{a,0}^b}{RT}} \right)^\beta.$$

Note that the current i is simply defined here as $i = -F \frac{dc_e}{dt}$ where c_e is the number of electrons per volume (in mol m^{-3})

4. Charge conservation equation

Let ρ be a charge density and j denote the current density, that is the flow of electric charge per unit of surface ($\text{C s}^{-1} \text{m}^{-2}$)

Question 7: *Explain why the equation*

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

is called the charge conservation equation.

We assume charge neutrality, that is ρ is constant and equal to zero, and 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 densities follows the Ohm law given by $j = \sigma E$, where σ is the conductivity in Siemens per meter (S m^{-1}), E is the electrical field and E derives from an electrical potential through the relation, $E = -\nabla \phi$.

Question 8: *Set up and solve the partial differential equation that governs this system and establish that*

$$U = RI,$$

for $U = \phi_L - \phi_R$, $I = -\int_L j \cdot n dS = \int_R j \cdot n dS$ and $R = \frac{L}{\sigma A}$.

Here, A is the area of the wire.

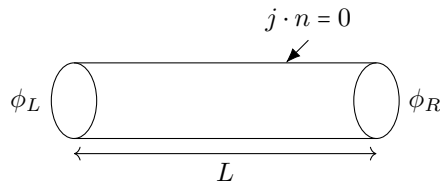


FIGURE 3. Illustration of a cylindrical wire with the applied boundary conditions.

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 are moving in the electrolyte. We assume also that the ion distribution in the electrolyte is homogeneous (the concentration are constant in space). It means in particular that we will consider a constant value of i_0 in (12). 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 it will look like for $t \geq 0$.

Question 9: *Find a relation between the potential drop $U = \phi_+ - \phi_-$ and the current I (of the form $U = f(I)$).*

To simplify expression (11), we take $\beta = \frac{1}{2}$. In fact, this is also the standard choice in applications.

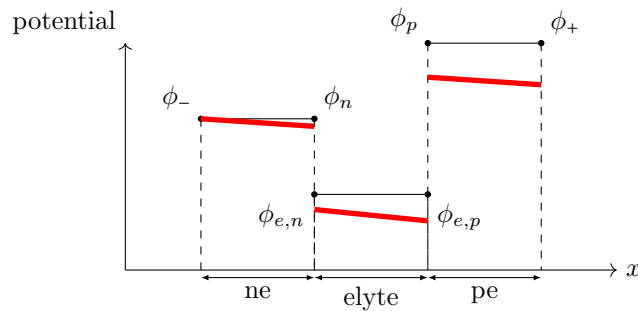


FIGURE 4. Illustration of the activation phase. We plot two configurations : $t < 0$ (black) and $t \geq 0$ (red). The current inside the battery is going from left to right from states of lower to higher electrical potential. This can be only be achieved by a energy contribution from battery which is given by the chemical reaction. Note the decrease of the net difference $\phi_+ - \phi_-$ decreases when the battery gets activated.

6. Ion transport in the electrolyte

A liquid electrolyte contains several ions (at least two of opposite charge in order to have charge neutrality) which move in the solution due the combined effects of an external electrical field and diffusion. For a ion indexed by i , we will consider the following expression for the flux N_i in $\text{mol m}^{-2} \text{s}^{-1}$,

$$(13) \quad N_i = -z_i u_i F c_i \nabla \phi - D_i \nabla c_i$$

where, for the ion i , z_i is the charge , u_i is the **mobility** (in $\text{m mol}^{-1} \text{s}^{-1}$), c_i is the concentration, D_i is the **diffusion coefficient**. By definition, the current density in a electrolyte is given as

$$(14) \quad j = F \sum_{i=1}^N z_i N_i.$$

On the right hand-side of (13), the first term is called the *migration* term and the second *diffusion term*. To understand the migration term $-z_i u_i F c_i \nabla \phi$, 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 tells us that the particle velocity will changed at a constant rate (we assume E constant). However, in an electrolyte, the charged ion will meet resistance at it encounters other molecules (charged

and neutral) whose resulting effect can be modeled as a friction force, $f_{\text{friction}} = -|q|\tau|v|$ where v is the velocity and τ some constant friction coefficient.

Question 10: *Relate the coefficient τ with the mobility. 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 a binary electrolyte with two ions of opposite charge. For example, in the electrolyte of a Lithium battery, we can have a Lithium ion Li^+ and a hexafluorophosphate ion PF_6^- . The governing equations are given by

$$(15a) \quad \frac{\partial c_+}{\partial t} = u_+ F \nabla \cdot (c_+ \nabla \phi) + D_+ \Delta c_+$$

$$(15b) \quad \frac{\partial c_-}{\partial t} = -u_- F \nabla \cdot (c_- \nabla \phi) + D_- \Delta c_-$$

and

$$(15c) \quad c_+ - c_- = 0.$$

The later equation expresses electrical neutrality.

Question 11: *Explain how the governing equations (15) are derived. Explain how (15c) follows from the charge conservation equation, $\nabla \cdot j = 0$, and (15a) and (15b).*

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 unknown in each domain are the electrical potential and the concentration of Lithium in its different form (LiC_6 , Li^+ and LiMnO), see Figure 5. The governing equations in the electrolyte are given in (15). In the electrodes, the lithium (LiC_6 and LiMnO) diffuses and the governing equations in these domains are given by mass conservation and charge conservation.

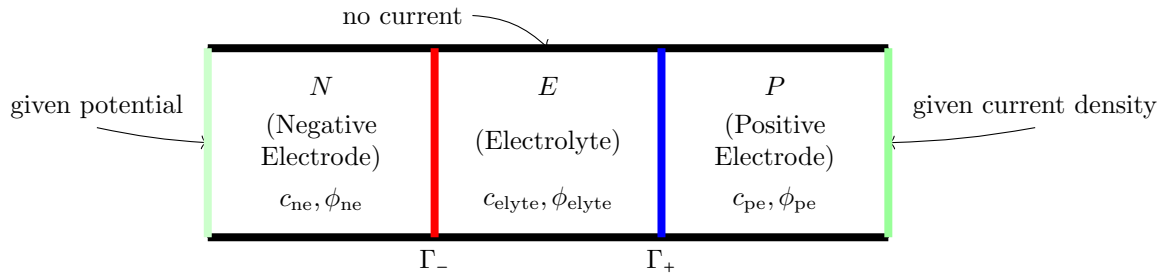


FIGURE 5. Battery model

Question 12: *Write the governing equations in each of the domain (P, N and E). Write down the boundary conditions and in particular the interface conditions at Γ_+ and Γ_- where the chemical reactions with either electron production or consumption occur.*

When we impose a uniform current and voltage at the sides and the initial conditions are also uniform, we have a one dimensional as treated configuration, as treated in Question 9. 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

$$(16) \quad c_\alpha(\bar{t}, x) = c_\alpha^0(x) + \varepsilon c_\alpha^1(\bar{t}, x), \quad \phi_\alpha(\bar{t}, x) = \phi_\alpha^0(x) + \varepsilon \phi_\alpha^1(\bar{t}, x)$$

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

Question 13: *Use the expansion above to obtain a linear approximation of the governing equations. Try to solve those numerically.*

8. Volume averaging method and tortuosity

The electrodes are porous to maximize interface area, see Figure 6. It is difficult to resolve all the geometry of this complicated interface. Therefore, we use a volume averaging method and compute effective quantities. To introduce the approach, let us consider a half-cell consisting a porous electrode material surrounded with the electrolyte. The domain consists then of two regions, also called phases (solid for the electrode, liquid for the electrolyte), which we denote as Ω_α where $\alpha \in \{\text{elde, elyte}\}$. For a given location \bar{x} , we consider a ball $B(\bar{x})$ centered in \bar{x} whose radius is chosen so that the ball provides a *representative elementary volume*. We denote the set of points of the phase α that are contained in the ball $B(\bar{x})$ as

$$B_\alpha(\bar{x}) = B(\bar{x}) \cap \Omega_\alpha.$$

For any scalar field u_α defined in the phase α , we define the *local volume average* and *intrinsic volume average* as

$$\overline{u_\alpha}(\bar{x}) = \frac{1}{V(\bar{x})} \int_{B_\alpha(\bar{x})} u_\alpha(x) dx \quad \text{and} \quad \langle u_\alpha(\bar{x}) \rangle = \frac{1}{V_\alpha(\bar{x})} \int_{B_\alpha(\bar{x})} u_\alpha(x) dx,$$

where $V(\bar{x})$ and $V_\alpha(\bar{x})$ are the volumes of $B(\bar{x})$ and $B_\alpha(\bar{x})$, respectively. The porosity of the phase α is naturally defined as

$$\varepsilon_\alpha(\bar{x}) = \frac{V_\alpha(\bar{x})}{V(\bar{x})}.$$

We have a representative elementary volume when the function $\varepsilon_\alpha(\bar{x})$ is smooth enough as a function of \bar{x} . We can compute a volume average formula for the gradient,

$$(17) \quad \overline{\nabla_x u_\alpha} = \nabla_{\bar{x}} \overline{u_\alpha} + \frac{1}{V} \int_{S(\bar{x})} u_\alpha(x) n(x) dS,$$

where $S(\bar{x})$ denotes the interface region between the two regions contained in the ball $B(\bar{x})$, that is $S(\bar{x}) = \partial\Omega_{\text{elde}} \cap \partial\Omega_{\text{elyte}} \cap B(\bar{x})$.

Question 14: *Derive formula (17).*

(We recall the generalization of the divergence theorem to gradient given by $\int_\Omega \nabla u dx = \int_{\partial\Omega} un dS$)

Let us focus first on a simple diffusion equation given by

$$(18) \quad \frac{\partial c_\alpha}{\partial t} + \nabla \cdot N_\alpha = 0 \quad \text{with} \quad N_\alpha = -D_\alpha \nabla c_\alpha.$$

Using volume averaging, we will end up with an effective model of the form

$$\frac{\partial(\varepsilon_\alpha \langle c_\alpha \rangle)}{\partial t} + \nabla \cdot \overline{N_\alpha} = 0,$$

where

$$\overline{N_\alpha} = -D_{\alpha, \text{eff}} \nabla \langle c_\alpha \rangle.$$

and $D_{\alpha, \text{eff}}$ is the *effective* diffusion coefficient. The effective diffusion coefficient relates to the *tortuosity* τ through the relation

$$D_{\alpha, \text{eff}} = \langle D_\alpha \rangle \frac{\varepsilon_\alpha}{\tau}.$$

Using (17), we obtain from (18), an expression of the form

$$(19a) \quad \overline{N_\alpha} = -\langle D_\alpha \rangle \nabla \overline{c_\alpha} - \Delta_\alpha$$

with

$$(19b) \quad \Delta_\alpha = \overline{D_\alpha \nabla c_\alpha} - \langle D_\alpha \rangle \nabla \overline{c_\alpha} + \langle D_\alpha \rangle \frac{1}{V} \int_{S(\bar{x})} c_\alpha n_\alpha dS.$$

Now, it is common to use an **empirical** relation of the form

$$\Delta_\alpha = D^* \langle D_\alpha \rangle \nabla \overline{c_\alpha}.$$

for a constant D^* .

Question 15: *If we assume a constant porosity, meaning that it does not depend on \bar{x} , give a relation between the tortuosity and the heuristic parameter D^* .*

Question 16: *Explain how the reaction contributions in the charge and mass balance equations, which occur at the interface (γ_\pm in Figure 5), can be transformed into a volumetric source.*

Question 17: *Write the governing equations in volume average form.*

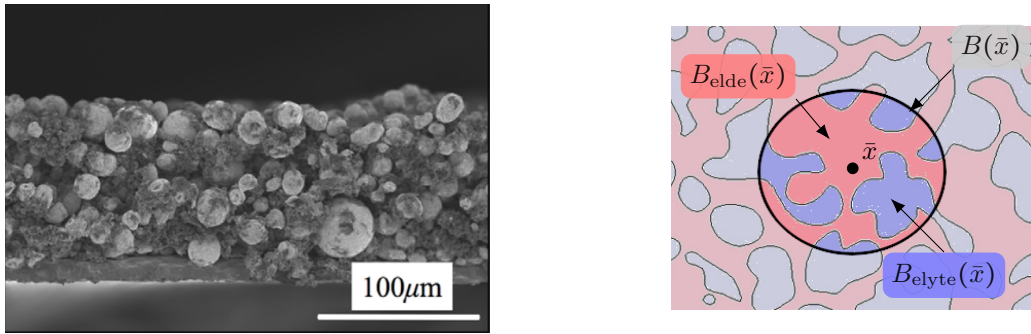


FIGURE 6. Metal oxide porous electrode (left). Schematic of the different domains used in the volume averaging approach (right).