Fick's Law and Double Capacitor Circuit

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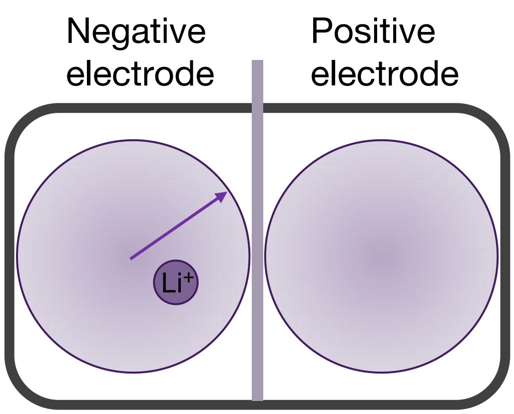
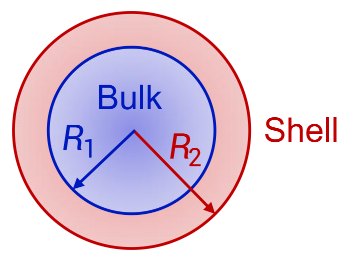
This note investigates the electrical analogy of the discretized Fick's law. As an example, we discretize the Fick's law equation along the radial direction, and the battery electrode is decomposed into two parts, i.e., the bulk and the shell (see Figure 1). We find the dynamics of the lithium-ion concentration in the bulk and shell regions are comparable to that of the capacitor voltage of the double capacitor circuit shown in Figure 2.

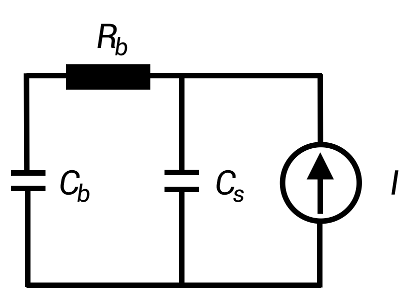


(a) Single particle model.

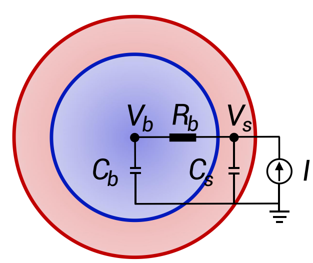


(b) Electrode decomposition into bulk and shell.

Figure 1: Diagram of single particle model.



(a) Double capacitor circuit.



(b) Circuit analogy for the negative electrode.

Figure 2: Diagram of double capacitor circuit.

1 Fick's Law

The Fick's law describes the lithium-ion diffusion inside of the electrode as follows

$$\frac{\partial c}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(Dr^2\frac{\partial c}{\partial r}\right).$$

Here, we decompose the electrode into the bulk and shell regions. In each region, the lithium-ion concentration can be expressed as

$$\begin{cases} c_b = \dfrac{1}{\Delta v_b}\displaystyle\int_0^{R_1} cdv, \\ c_s = \dfrac{1}{\Delta v_s}\displaystyle\int_{R_1}^{R_2} cdv, \end{cases}$$

where c_b is the concentration in the bulk region, c_s the shell region, $\Delta v_b = \frac{4\pi R_1^3}{3}$, and $\Delta v_s = \frac{4\pi R_2^3}{3} - \frac{4\pi R_1^3}{3}$, respectively. Therefore, the dynamics of lithium-ion concentration $\frac{\partial c}{\partial t} := \dot{c}$ in each region follows

$$\begin{aligned} \dot{c}_b &= \frac{1}{\Delta v_b}\int_0^{R_1} \dot{c}dv \\ &= \frac{1}{\Delta v_b}\int_0^{R_1} \frac{1}{r^2}\frac{\partial}{\partial r}\left(Dr^2\frac{\partial c}{\partial r}\right) d\frac{4\pi r^3}{3} \\ &= \frac{1}{\Delta v_b}\int_0^{R_1} d\left(4\pi Dr^2\frac{\partial c}{\partial r}\right) \\ &= \frac{1}{\Delta v_b}\left(4\pi DR_1^2 \left.\frac{\partial c}{\partial r}\right|_{R_1}\right), \end{aligned}$$

and

$$\begin{aligned} \dot{c}_s &= \frac{1}{\Delta v_s}\int_{R_1}^{R_2} \dot{c}dv \\ &= \frac{1}{\Delta v_s}\left(4\pi DR_2^2 \left.\frac{\partial c}{\partial r}\right|_{R_2} - 4\pi DR_1^2 \left.\frac{\partial c}{\partial r}\right|_{R_1}\right). \end{aligned}$$

In view of $\left.\frac{\partial c}{\partial r}\right|_{R_1} = \frac{c_s - c_b}{R_2/2}$ and $\left.\frac{\partial c}{\partial r}\right|_{R_2} = -\frac{J}{D}$, we can build $\dot{c}_b$ and $\dot{c}_s$ in terms of J as follow

$$\begin{cases} \dot{c}_b = -\dfrac{8\pi DR_1^2}{\Delta v_b R_2}c_b + \dfrac{8\pi DR_1^2}{\Delta v_b R_2}c_s, \\ \dot{c}_s = \dfrac{8\pi DR_1^2}{\Delta v_s R_2}c_b - \dfrac{8\pi DR_1^2}{\Delta v_s R_2}c_s - \dfrac{4\pi R_2^2}{\Delta v_s}J. \end{cases}$$

If we build them in terms of I, they are

$$\begin{cases} \Delta v_b^* \dot{c}_b = \dfrac{c_s - c_b}{R_D}, & \text{(1a)} \\ \Delta v_s^* \dot{c}_s = \dfrac{c_b - c_s}{R_D} - I, & \text{(1b)} \end{cases}$$

for the positive electrode since $J = \frac{I}{FS}$ (suppose $I > 0$ for charge), and

$$\begin{cases} \Delta v_b^* \dot{c}_b = \dfrac{c_s - c_b}{R_D}, & \text{(2a)} \\ \Delta v_s^* \dot{c}_s = \dfrac{c_b - c_s}{R_D} + I, & \text{(2b)} \end{cases}$$

for the negative electrode because $J = -\frac{I}{FS}$ (suppose $I > 0$ for charge), where $\Delta v_b^* = \frac{FS\Delta v_b}{4\pi R_2^2}$, $\Delta v_s^* = \frac{FS\Delta v_s}{4\pi R_2^2}$, and $R_D = \frac{R_2^3}{2FSDR_1^2}$, respectively.

2 Double Capacitor Circuit

The double capacitor circuit is shown in Figure 2. Suppose $I > 0$ for charge. The dynamics of V_b and V_s can be expressed as

$$\begin{cases} C_b \dot{V}_b = \dfrac{V_s - V_b}{R_b}, & \text{(3a)} \\ C_s \dot{V}_s = \dfrac{V_b - V_s}{R_b} + I, & \text{(3b)} \end{cases}$$

where V_b is the voltage across C_b, and V_s the voltage across C_s, respectively.

3 Discussion

From above, we can see that the discretized Fick's law and the resultant electrode can be represented using an electrical circuit—the double capacitor circuit. In view of (2) and (3), c_b and c_s in the negative electrode follow the same dynamics of V_b and V_s in the double capacitor circuit, and

$$\begin{aligned} C_b &= \Delta v_b^* = \frac{FS\Delta v_b}{4\pi R_2^2}, \\ C_s &= \Delta v_s^* = \frac{FS\Delta v_s}{4\pi R_2^2}, \\ R_b &= R_D = \frac{R_2^3}{2FSDR_1^2}. \end{aligned}$$