Fick's Law and Double Capacitor Circuit

Ning Tian

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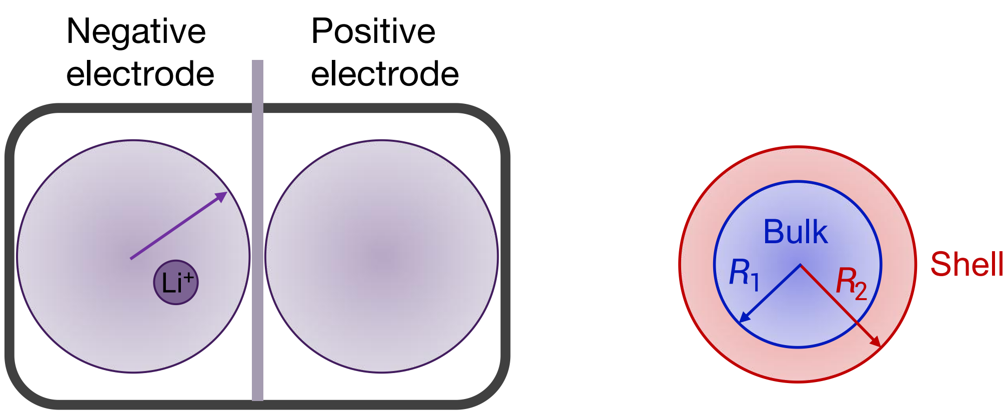
This note invesitigates the resemblance between discretized Fick's law and an electrical circuit. Specifically, the Fick's law equation is discretized along the radial direction into two parts, i.e., the bulk and the shell (see Figure 1). The dynamics of the lithium-ion concentration in the bulk and shell regions are the same with that of the voltage across the two capacitors in the double capacitor circuit (see Figure 2).



(a) Single Particle Model. (b) Electrode decomposition into bulk and shell.

Figure 1: Diagram of Single Particle Model.

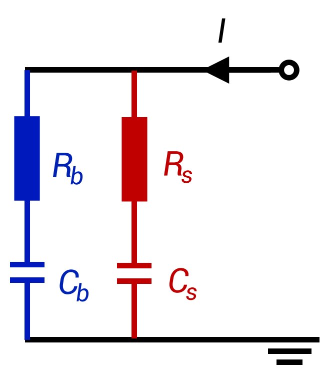


Figure 2: Diagram of a Double Capacitor Circuit.

1 Fick's Law

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

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

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

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

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 $\Delta v_s = \frac{4\pi R_2^3}{3} - \frac{4\pi R_1^3}{3}$. 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

$$\begin{cases} \dot{c}_b = \dfrac{-1}{\frac{FS\Delta v_b}{4\pi R_2^2}\frac{R_2^3}{2FSDR_1^2}}c_b + \dfrac{1}{\frac{FS\Delta v_b}{4\pi R_2^2}\frac{R_2^3}{2FSDR_1^2}}c_s, & \text{(1a)} \\ \dot{c}_s = \dfrac{1}{\frac{FS\Delta v_s}{4\pi R_2^2}\frac{R_2^3}{2FSDR_1^2}}c_b + \dfrac{-1}{\frac{FS\Delta v_s}{4\pi R_2^2}\frac{R_2^3}{2FSDR_1^2}}c_s - \dfrac{1}{\frac{FS\Delta v_s}{4\pi R_2^2}}I, & \text{(1b)} \end{cases}$$

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

$$\begin{cases} \dot{c}_b = \dfrac{-1}{\frac{FS\Delta v_b}{4\pi R_2^2}\frac{R_2^3}{2FSDR_1^2}} c_b + \dfrac{1}{\frac{FS\Delta v_b}{4\pi R_2^2}\frac{R_2^3}{2FSDR_1^2}} c_s, & \text{(2a)} \\ \dot{c}_s = \dfrac{1}{\frac{FS\Delta v_s}{4\pi R_2^2}\frac{R_2^3}{2FSDR_1^2}} c_b + \dfrac{-1}{\frac{FS\Delta v_s}{4\pi R_2^2}\frac{R_2^3}{2FSDR_1^2}} c_s + \dfrac{1}{\frac{FS\Delta v_s}{4\pi R_2^2}} I, & \text{(2b)} \end{cases}$$

for the negative electrode because $J = -\frac{I}{FS}$ (suppose $I > 0$ for charge).

2 Double Capacitor Circuit

Suppose $I > 0$ for charge. The dynamics of V_b and V_s is

$$\begin{cases} \dot{V}_b = \dfrac{-1}{C_b(R_b + R_s)} V_b + \dfrac{1}{C_b(R_b + R_s)} V_s + \dfrac{R_s}{C_b(R_b + R_s)} I, \\ \dot{V}_s = \dfrac{1}{C_s(R_b + R_s)} V_b + \dfrac{-1}{C_s(R_b + R_s)} V_s + \dfrac{R_b}{C_s(R_b + R_s)} I. \end{cases}$$

By assuming $R_s = 0$, we have

$$\begin{cases} \dot{V}_b = \dfrac{-1}{C_b R_b} V_b + \dfrac{1}{C_b R_b} V_s, & \text{(3a)} \\ \dot{V}_s = \dfrac{1}{C_s R_b} V_b + \dfrac{-1}{C_s R_b} V_s + \dfrac{1}{C_s} I. & \text{(3b)} \end{cases}$$

3 Conclusion

In view of (2) and (3), we can see that c_b and c_s in the negative electrode follows the same dynamics of V_b and V_s in the double capacitor circuit, and

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