

Electrochemical Energy Storage

In this lecture, we will learn some examples of electrochemical energy storage. A general idea of electrochemical energy storage is shown in Figure 1. When the electrochemical energy system is connected to an external source (connect OB in Figure 1), it is charged by the source and a finite charge Q is stored. So the system converts the electric energy into the stored chemical energy in charging process. When the system is connected to an external resistive circuit (connect OA in Figure 1), it releases the finite Q and drives a current through the external circuit. The system converts the stored chemical energy into electric energy in discharging process.

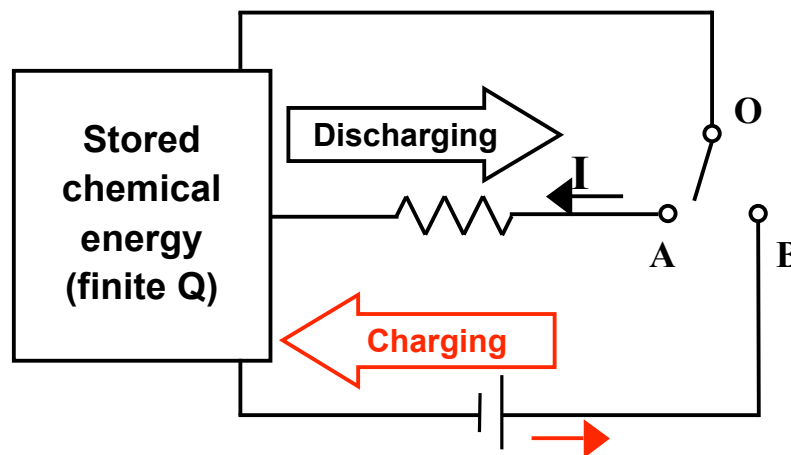


Figure 1: Electrochemical Energy Storage

A simple example of energy storage is capacitor. Figure 2 shows the basic circuit for capacitor discharge. Here we talk about the integral capacitance. The capacitance is defined as a constant

$$C = \frac{Q}{V_C} \quad (1)$$

The current is

$$I = -\frac{dQ}{dt} = -C \frac{dV_C}{dt} \quad (2)$$

The voltage applied to the external resistance is

$$V = \frac{Q}{C} - IR_{\text{int}} = IR_{\text{ext}} \quad (3)$$

Plug (1) and (2) into (3) and use the total resistance $R = R_{\text{int}} + R_{\text{ext}}$, then we get

$$Q = -RC \frac{dQ}{dt} \quad (4)$$

Apply the initial condition $Q(t=0) = Q_0$, we can solve the equation

$$Q = Q_0 e^{-\frac{t}{RC}} \quad (5)$$

The relation between stored charge and time is shown in Figure 3, where $\tau = RC$ is called decay time.

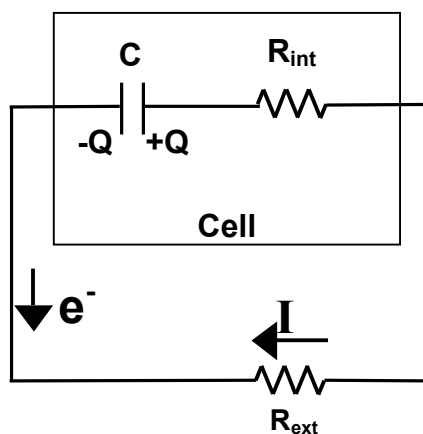


Figure 2: Basic Circuit for Capacitor Discharge

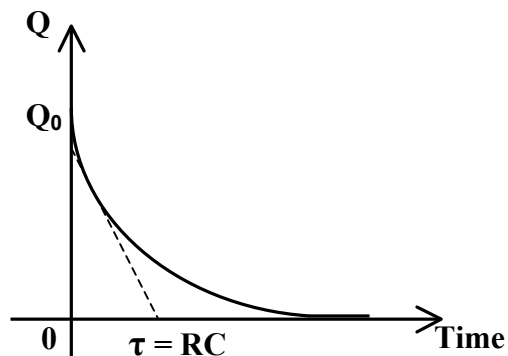


Figure 3: Stored Charge vs. Time for Capacitor

In the following sections, we will introduce some practical examples of electrochemical energy storage.

1. Supercapacitors

A supercapacitor (or ultracapacitor) is an electrochemical capacitor that has an unusually high energy density when compared to common capacitors, typically on the order of thousands of times greater than a high capacity electrolytic capacitor. In general, supercapacitors improve storage density through the use of a nano porous material, as shown in Figure 4. Two very high surface area porous electrodes are soaked in electrolyte. The charge is stored in electrochemical double layers.

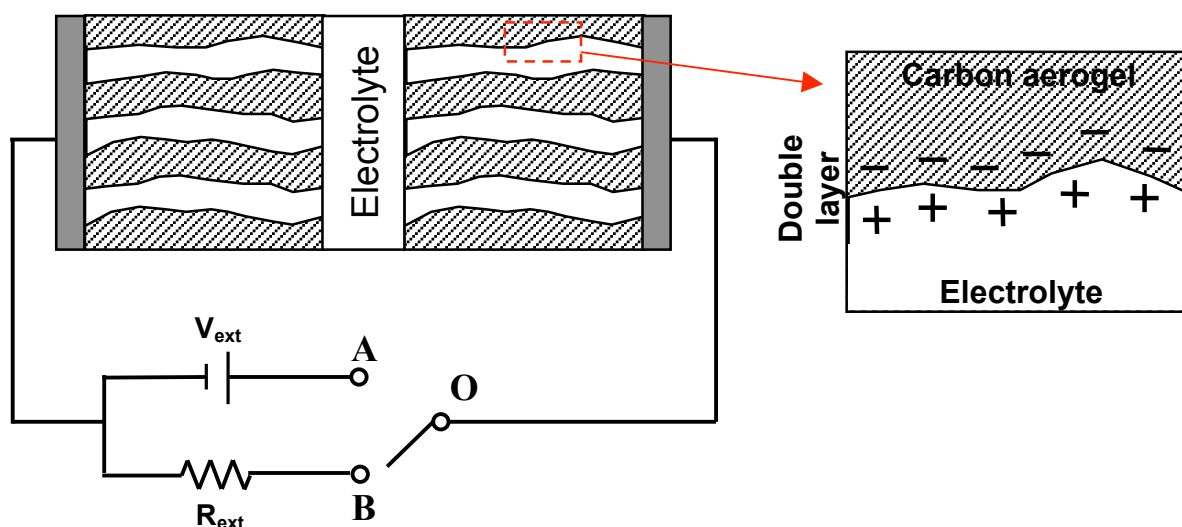


Figure 4: Basic Structure of Supercapacitor

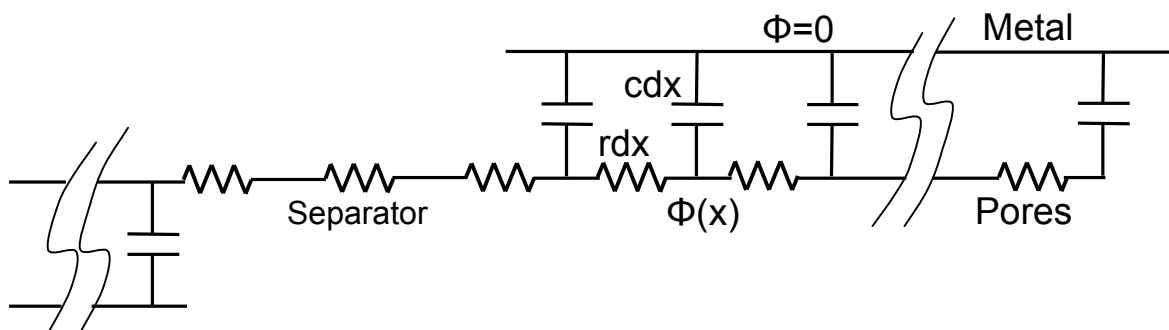


Figure 5: Equivalent Circuit of Supercapacitor

A supercapacitor can be modeled as an RC transmission line, shown in Figure 5. Assume a symmetric situation of two identical porous electrodes of thickness L , and thus focus on only one, in the region $0 < x < L$. The electrolyte-filled pore space has a constant volume-averaged resistance per length r and constant capacitance per unit length c . Neglect any resistance in the porous electrode or the thin gap between the electrodes. The mean potential in the pores satisfies a linear diffusion equation

$$rc \frac{\partial \phi}{\partial t} = \frac{\partial^2 \phi}{\partial x^2} \quad (6)$$

If we apply a sudden change of voltage V for $t > 0$ at $x=0$, the current response can be estimated as

$$I \sim \begin{cases} V \sqrt{\frac{c}{rt}} & , t \ll rcL^2 \\ \frac{V}{rL} e^{-\frac{t}{rcL^2}} & , t \gg rcL^2 \end{cases}$$

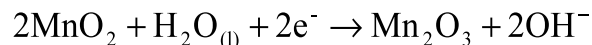
2. Primary Batteries

A primary cell is any kind of battery in which the electrochemical reaction is not reversible. Primary batteries can produce current immediately on assembly. A primary cell is not rechargeable because the chemical reactions are not reversible and active materials may not return to their original forms. Leclanche cell is a typical primary battery. The modern commercial Leclanche cell packaging and the basic structure are shown in Figure 6. The detailed reactions are

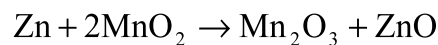
Anode (oxidation reaction, produces electrons):



Cathode (reduction reaction, consumes electrons):



Net reaction:



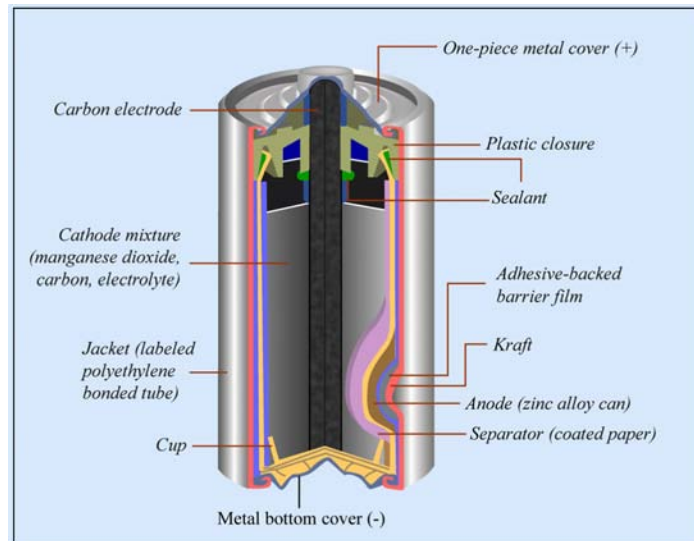


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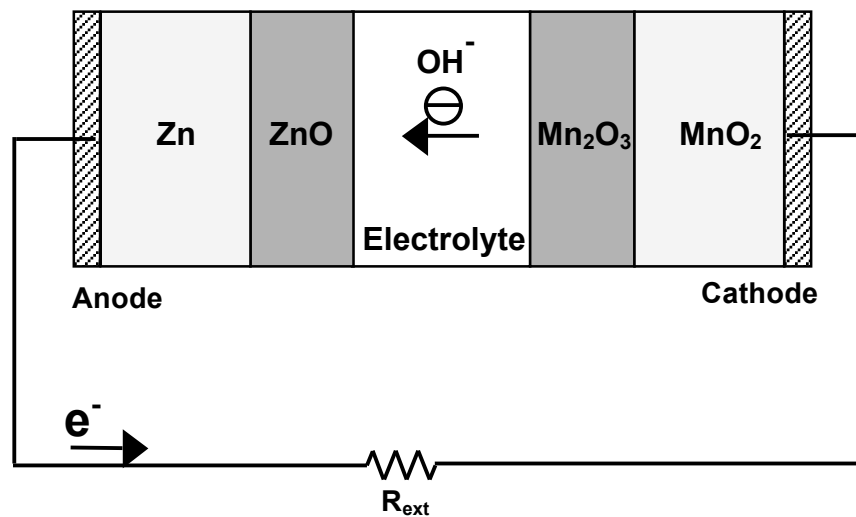
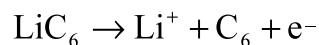


Figure 6: Basic Structure and Packaging [1] of LeClanche Cell

3. Secondary Batteries

Secondary batteries are also known as rechargeable batteries because their electrochemical reactions are electrically reversible. Li-ion battery shown in Figure 7 is a typical example of secondary battery. Li ions move from the negative electrode to the positive electrode during discharge, and reversely when charging. During discharge the negative electrode is the anode where oxidation takes place and during charge it turns into the cathode where reduction takes place. The half-reactions of discharging are

Anode (oxidation reaction, produces electrons):



Cathode (reduction reaction, consumes electrons):

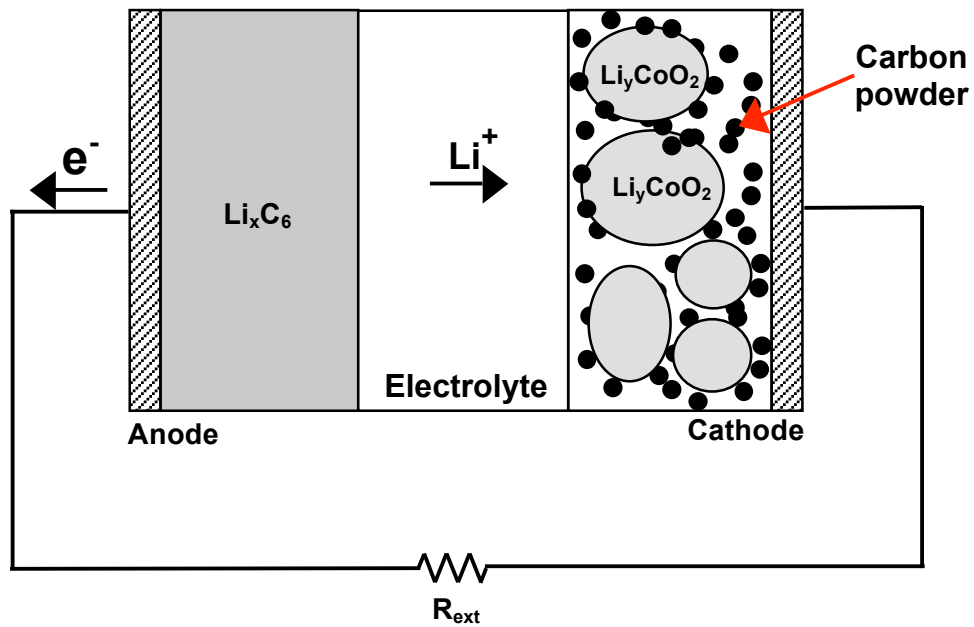
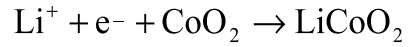


Figure 7: Basic Structure of Li-ion Battery

Discharging and charging of a simple secondary battery can be modeled as Figure 8.

1) Discharging (connect OA in Figure 8):

$$\left\{ \begin{array}{l} I = -\frac{dQ_a}{dt} = \frac{dQ_c}{dt} = \frac{V_a^0(Q_a) + V_c^0(Q_c)}{R} \\ Q_a(t=0) = Q_a^0 \\ Q_c(t=0) = 0 \end{array} \right.$$

2) Charging (connect OB in Figure 8):

$$I = \frac{V_a^0(Q_a) + V_c^0(Q_c) - V_{ext}}{R} < 0$$

where R is the total resistance $R = R_{int} + R_{ext}$.

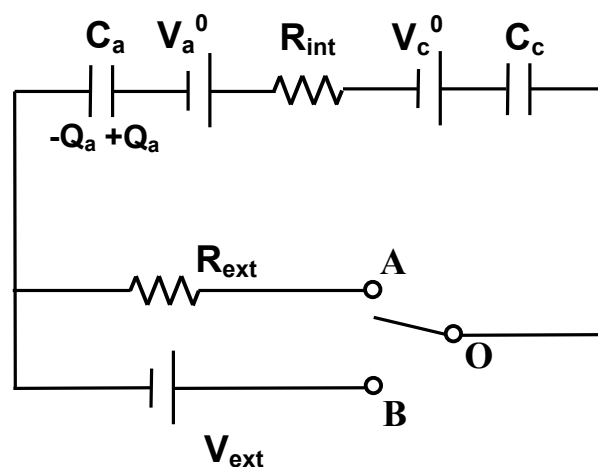
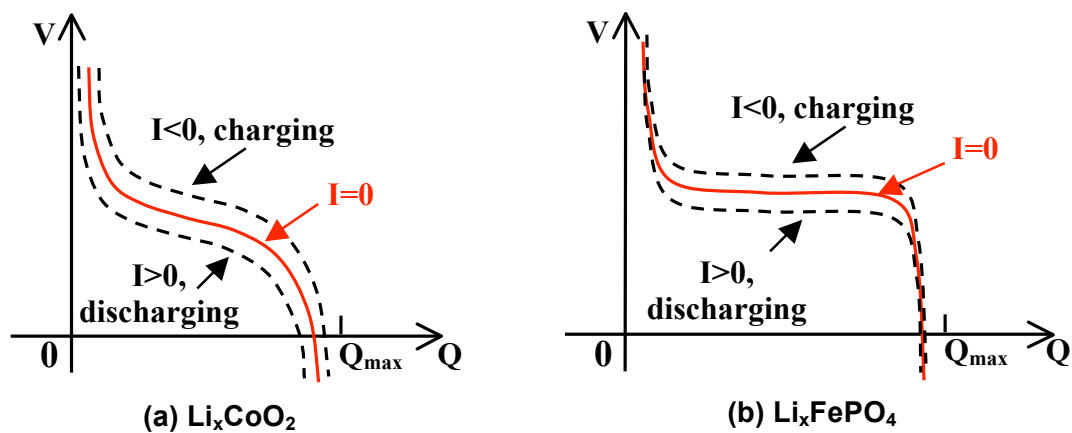


Figure 8: Equivalent Circuit of Rechargeable Battery

The relation between V and Q of Li-ion battery is often highly nonlinear, as shown in Figure 9. The detail will be discussed in Lecture 9.

Figure 9: Nonlinear V vs. Q Relation of Li-ion Batteries

Source: <http://ocw.mit.edu/courses/chemical-engineering/10-626-electrochemical-energy->

[systems-spring-2011/lecture-notes/MIT10_626S11_lec03.pdf](http://ocw.mit.edu/courses/chemical-engineering/10-626-electrochemical-energy-systems-spring-2011/lecture-notes/MIT10_626S11_lec03.pdf)