Lecture 4: Dynamics of Equivalent Circuits

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1. Simple Equivalent Circuit for a Battery

Batteries have a finite charge capacity Q_{max}. So the open circuit voltage is dependent upon the current charge state Q. Figure 1 shows a typical dependence of the open circuit voltage as a function of charge and the current. A simple equivalent circuit for a battery can thus be written as

$$V = V_o(Q) - \eta(I,Q) = IR_{\text{ext}} \tag{1}$$

where V_o is the open circuit voltage and η is the cell overpotential (relative to the equilibrium), which is a positive voltage loss for a positive (galvanic) current I>0, and negative for a negative (electrolytic) current I<0. This model assumes that the voltage depends only on the instantaneous current and state of charge, and not on the prior history (via various internal relaxation phenomena, such as diffusion, which we will discuss later in the class).

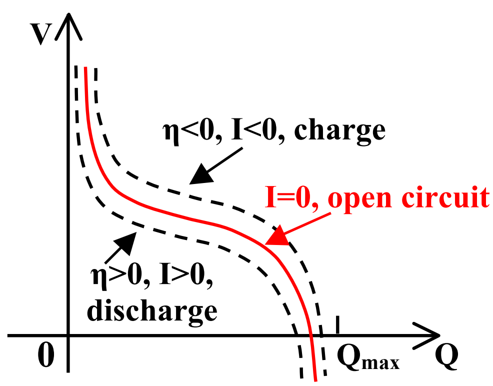


Figure 1: Typical "discharge curve" for a battery, showing the cell voltage versus state of charge at different currents.

2. Linear response

When a small perturbation is applied to the equivalent circuit, for example a small voltage step or current step, the response of the circuit can be estimated by linearization. Given $V(I,Q)$, we assume the perturbations of charge and current are small. So we have

$$\begin{cases} Q = Q_0 + \Delta Q \\ I = I_0 + \Delta I \end{cases} \tag{13}$$

where $\begin{cases} |\Delta Q| << Q_0 \\ |\Delta I| << I_0 \end{cases}$.

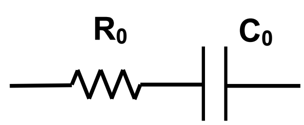
By Taylor expansion, $V(I,Q)$ can be linearized at $\begin{cases} Q = Q_0 \\ I = I_0 \end{cases}$ as

$$\Delta V = \left.\frac{\partial V}{\partial Q}\right|_{Q_0, I_0} \Delta Q + \left.\frac{\partial V}{\partial I}\right|_{Q_0, I_0} \Delta I \tag{14}$$

Define differential internal resistance $R_0 = \left.\frac{\partial V}{\partial I}\right|_{Q_0, I_0}$ and differential cell capacitance $\frac{1}{C_0} = \left.\frac{\partial V}{\partial Q}\right|_{Q_0, I_0} = \left(\frac{dV_O}{dQ} - \frac{\partial \eta}{\partial Q}\right)_{Q_0, I_0}$, we write (10) as

$$\Delta V = \frac{1}{C_0}\Delta Q + R_0 \frac{d\Delta Q}{dt} \tag{15}$$

The equivalent circuit for linear response is



3. Nonlinear response

To illustrate the possible nonlinear electrical response of a battery, let us consider different common modes of discharge.

3.1 Constant Current

When discharging at a constant current, the state of charge Q (defined here as the integral of Galvanic current I>0) increases linearly with time.

$$Q = Q_0 + It \tag{2}$$

Assuming the overpotential is only a function of current and charge, equation (1) now can be written as

$$V(t) = V_o(Q_0 + It) - \eta(I, Q_0 + It) = IR_{\text{ext}}(t) \tag{3}$$

Equation (3) also tells us the time-dependent external resistance R_{ext} required to maintain constant current discharge. Note that the battery voltage, V(t), external resistance, R(t)=V(t)/I and electrical power P(t)=I V(t) all have the same time dependence at constant current.

In constant current mode, the "C rate" is used to describe battery discharging. The C rate is defined as

$$C \ \ \text{rate} = \frac{\text{total} \ \ \text{capacity}}{\text{n} \ \ \text{hours}} = \frac{C}{n}$$

So, "C/2" means the battery discharges total capacity in 2 hours. "60C" means the battery discharges its total capacity in 1 minute. The C rate can be somewhat ambiguous, since the full capacity is rarely used (or would require too much time or energy). The nominal capacity Q_{max} is reached when the reactants have been entirely used at the capacity-limiting electrode, and the voltage drops to zero. The practical capacity, however, is usually defined by the state of charge where the voltage drops below a useful threshold, such as 50% of the initial open circuit voltage.

3.2 Constant Load

For discharging at a constant load, the external resistance is fixed while both the current and voltage vary with time. Using the definition of current $I = \frac{dQ}{dt}$, equation (1) becomes

$$V(t) = V_o(Q) - \eta(\frac{dQ}{dt}, Q) = \frac{dQ}{dt} R_{\text{ext}} \tag{4}$$

This is first-order nonlinear ODE, which can be solved for dQ/dt and integrated to obtain Q(t) and thus V(t) . If the differential internal resistance $R_{int}(Q)$ depends only on the state of charge (i.e. the overpotential is linear in current), then we have

$$V = V_O(Q) - \frac{dQ}{dt} R_{int}(Q) = \frac{dQ}{dt} R_{ext}$$

This is a first-order separable ODE

$$\frac{dQ}{dt} = \frac{V_O(Q)}{R_{ext} + R_{\text{int}}(Q)} \tag{5}$$

which can be solved in implicit form:

$$\int_{Q_0}^{Q} \frac{(R_{ext} + R_{\text{int}}(Q))dQ}{V_o(Q)} = -\int_0^t dt = -t \tag{6}$$

Example: Consider a battery with a constant internal resistance and open circuit voltage $V_O(Q) = V^0(1 - \left(\frac{Q}{Q_{\max}}\right)^2)$ which is discharged through a constant external resistance starting from Q=0 at t=0. Let $R = R_{int} + R_{ext}$ be the total resistance of the equivalent circuit. Performing the integral above, we find

$$Q(t) = Q_{\max} \tanh\left(\frac{V^0 t}{RQ_{\max}}\right)$$

$$I(t) = \frac{dQ}{dt} = \frac{V^0 Q_{\max}}{R} \operatorname{sech}^2\left(\frac{V^0 t}{RQ_{\max}}\right)$$

Note that the time scale for discharge is RC, where the effective capacitance is $C = Q_{max}/V^0$ (which we could have anticipated by dimensional analysis).

We can also eliminate time in the preceding equations to relate voltage V to charge Q during the discharge at constant load to obtain:

$$V = IR_{ext} = \frac{V^0(Q)}{1 + R_{\text{int}} / R_{ext}}$$

The voltage does not drop off as quickly at constant load compared to constant current, since the current decays with time (at the RC time scale). The full capacity is also reached at constant load, albeit slowly in the final stages, as the current decays to zero.

3.3 Constant Power

Discharge can also occur at a constant power,

$$P = IV = \text{constant} \tag{7}$$

Now the voltage will drop off even faster than at constant current, since the current must be increased with time to compensate for the decreasing voltage, in order to maintain constant power.

In constant power mode, the "E rate" is often used to describe battery energy delivery in discharging. E rate is defined as

$$\text{E rate} = \frac{\text{total stored energy}}{\text{n hours}} = \frac{\text{E}}{\text{n}}$$

So, "E/2" means the battery delivers total stored energy in 2 hours. "60E" means the battery delivers total stored energy in 1 minute.

Plug (1) into (7), we get,

$$P = \left[V_0(Q) - \eta\left(\frac{dQ}{dt}, Q\right) \right]\left(\frac{dQ}{dt} \right) \tag{8}$$

This is a nonlinear ODE for *Q(t)*. It can be solved by first obtaining dQ/dt as a function of Q, which is a first order separable ODE.

Example: Consider again a battery with open circuit voltage $V_O(Q) = V^0\left(1 - \left(\frac{Q}{Q_{\max}}\right)^2\right)$ but now neglect the internal resistance and discharge at constant power P. Integrating Eq (8), we obtain an implicit solution for Q(t):

$$Pt = V^0 Q_{\max}\left(\frac{Q}{Q_{\max}} - \frac{1}{3}\left(\frac{Q}{Q_{\max}} \right)^3 \right)$$

We see that Q grows linearly with time at first and then switches to cube root of time

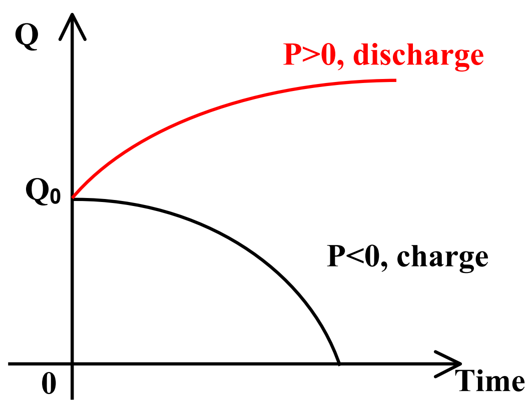


Figure 2: Q vs. time in constant power mode

The three different modes of discharge are summarized in figure 3. For a similar initial current and voltage at Q=0, we see that the voltage drops more quickly at constant power (P), than at constant current (I), than constant resistance (R). The useable capacity (defined here as total charge Q released when voltage drops to zero) is smallest for constant power. At constant current, the capacity is larger, but still less than the maximum. In order to reach the maximum capacity, the current must decay to zero, as in the case of constant external resistance.

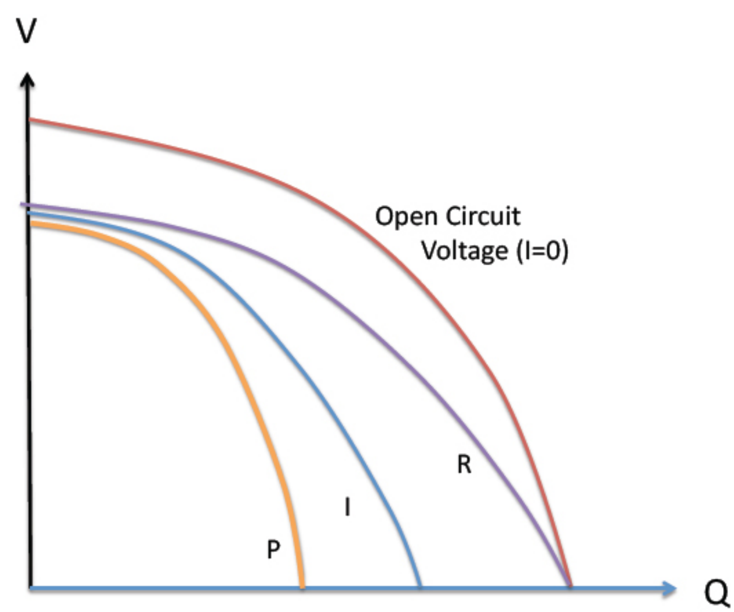


Fig 3. Battery discharge at constant power (P), constant current (I), and constant external resistance (R), compared to open circuit voltage versus state of charge.