

# I. Equivalent Circuit Models

## Lecture 1: Basic Physics of Galvanic Cells

Notes by MIT Student (and MZB)

In this lecture, we give an overview of electrochemical cell operations, and define basic terminologies frequently used in a discussion of electrochemical cell operations.

### 1. Electrochemical Cells and Their Operations

*Faradaic Reaction* : An electrochemical reaction that involves charge transfer

*Electrochemical Cell* : Two half reactions involving charge transfer, connected via an electrolyte (conducting ions) and an external circuit (conducting electrons)

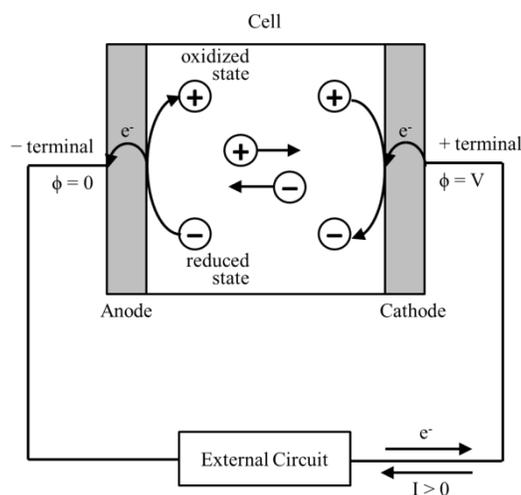


Figure 1. Galvanic Operation of an Electrochemical Cell

In a *galvanic cell*, electrons and ions flow spontaneously, converting chemical energy into electrical energy (and heat). As shown in Figure 1, in galvanic cell operation, an oxidation reaction occurs at anode, producing electrons. On the other hand, at cathode, a reduction reaction occurs, consuming electrons on the electrode surface. Since the electrons are not able to move through the electrolyte, they flow via external circuits from anode to cathode, making a current in a direction from cathode to anode. In electrolyte phase, oxidized species migrates from anode to cathode, and reduced species migrates from cathode to anode in net amount, respectively. In

an *electrolytic cell*, charges flow in the opposite direction, driven by an external voltage which inputs electrical energy to be stored as chemical energy. The sign convention of current is defined to have a positive sign for galvanic cells. Therefore, in an electrolytic cell operation, a current has a negative value.

The followings are two examples of electrochemical cell construction:

Example 1: PEM fuel cell

|              |                                                       |
|--------------|-------------------------------------------------------|
| Anode        | $H_2(g) \rightarrow 2H^+ + 2e^-$                      |
| Cathode      | $\frac{1}{2}O_2(g) + 2H^+ + 2e^- \rightarrow H_2O(l)$ |
| Net Reaction | $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$      |
| Electrolyte  | polymer electrolyte membrane (PEM)                    |

Example 2: Li-ion battery

|              |                                                                     |
|--------------|---------------------------------------------------------------------|
| Anode        | $LiC_6 \rightarrow Li^+ + e^- + C_6$                                |
| Cathode      | $Li^+ + e^- + CoO_2 \rightarrow LiCoO_2$                            |
| Net Reaction | $LiC_6 + CoO_2 \rightarrow LiCoO_2 + C_6$ (“rocking chair battery”) |
| Electrolyte  | organic liquid containing $LiPF_6$ salt dissolved                   |

## 2. Equivalent Circuit

It is possible to represent an electrochemical cell using an equivalent circuit model. We will learn how to model physical components of an electrochemical cell with circuit element representations later on in this course. For now, we focus on operation behaviors of circuits, given an equivalent circuit model of an electrochemical cell.

A galvanic cell can be represented by an equivalent circuit as following:

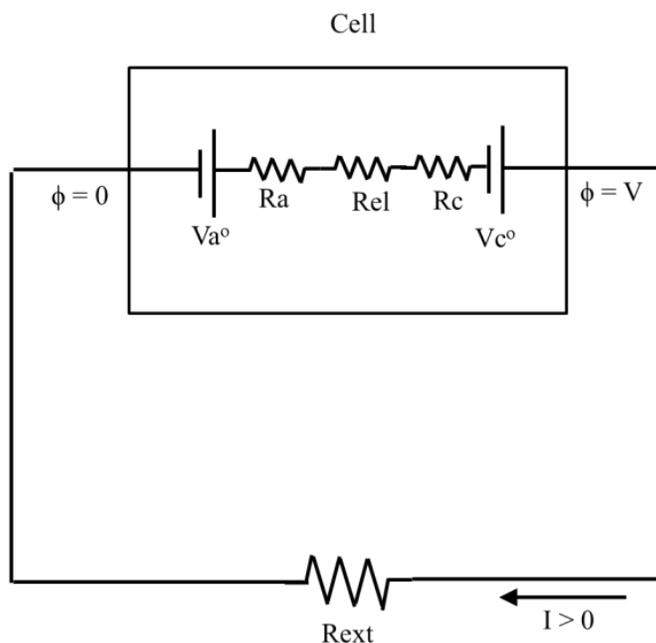


Figure 2. An Equivalent Circuit Model of a Galvanic Cell

where

- $V_a^o$  : Standard Equilibrium Half-cell Potential of Anode
- $V_c^o$  : Standard Equilibrium Half-cell Potential of Cathode
- $R_a$  : Interface Resistance at Anode
- $R_c$  : Interface Resistance at Cathode
- $R_{el}$  : Resistance through Electrolyte
- $R_{ext}$  : External Circuit Resistance

Equivalently, the above equivalent circuit may be simplified by lumping circuit elements into fewer representative elements.

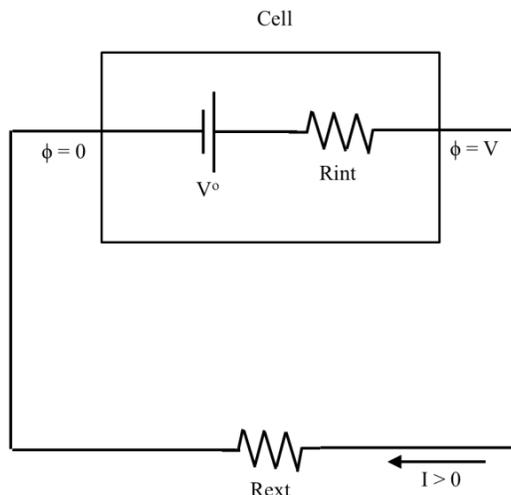


Figure 3. Lumped Equivalent Circuit Model of a Galvanic Cell

Where  $V_o = V_c^o - V_a^o$  : Open Circuit Voltage (OCV) of a Cell  
 $R_{int} = R_a + R_{el} + R_c$  : Internal Resistance

Note that standard equilibrium half-cell potentials ( $V_a^o$ , and  $V_c^o$ ) are sometimes denoted  $E^o$  in electrochemistry, but that notation is refrained since it may be confusing with an electric field. The standard equilibrium half-cell potentials may be either positive or negative, as long as  $V_o$ , open circuit voltage, is positive (for a galvanic cell).

According to the Kirchhoff's law,

$$V = IR_{ext} = V_o - IR_{int} \quad (1)$$

where  $V$  is the *cell voltage*. The cell voltage is a function of current,  $I$ , state of charge,  $Q$ , which will be defined in Lecture 3, and other electrochemical variables. The cell voltage, in thermodynamic terms, means the free energy difference of net cell reaction per charge transferred. The thermodynamic interpretation of cell voltage will be discussed in Lecture 7.

$$V(I, Q, \dots) = \frac{\Delta G}{ne} = \frac{[\text{free energy difference of net reaction}]}{[\text{charge transferred}]} \quad (2)$$

When the external resistance is zero, we obtain *short circuit current*:

$$I_s = \frac{V_o}{R_{int}} \quad (3)$$

Given a current and a cell voltage, we can calculate a *cell power*,  $P$ , which is electrical work done by cell per unit time.

$$P = IV \quad (4)$$

Assuming a constant internal resistance, the dependence of cell voltage and cell power to the current can be plotted as following:

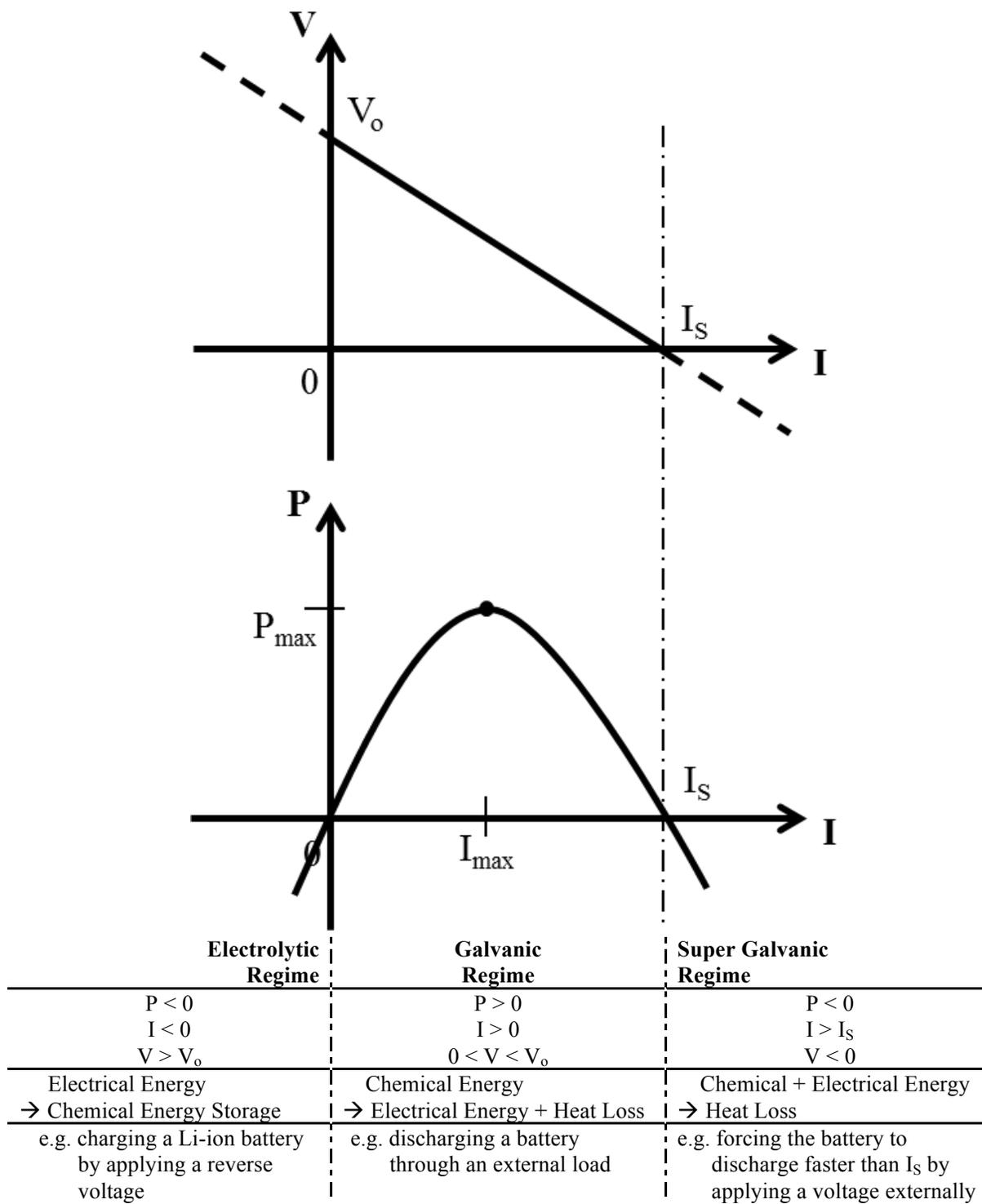


Figure 4. Cell Voltage and Power Behavior as a Function of Current

Table 1. Different Regimes of Cell Operation and Features

More realistic fuel cells do not have constant internal resistance. Rather, they have nonlinear contributions from several overpotential components. *Overpotential* refers to the magnitude of potential drop caused by resistance to the passage of current. We will learn their behaviors and interpretations through this course.

Cell voltages of typical fuel cells show the following dependence on current. With a small current, activation overpotential dominates and gives the concave curve in the beginning. Following that, the resistance from either electron or ion transport becomes the limiting factor, giving the linear curve in the middle. Lastly, when current is large enough, transport of fuel cannot sustain the current, and the cell voltage drops quickly.

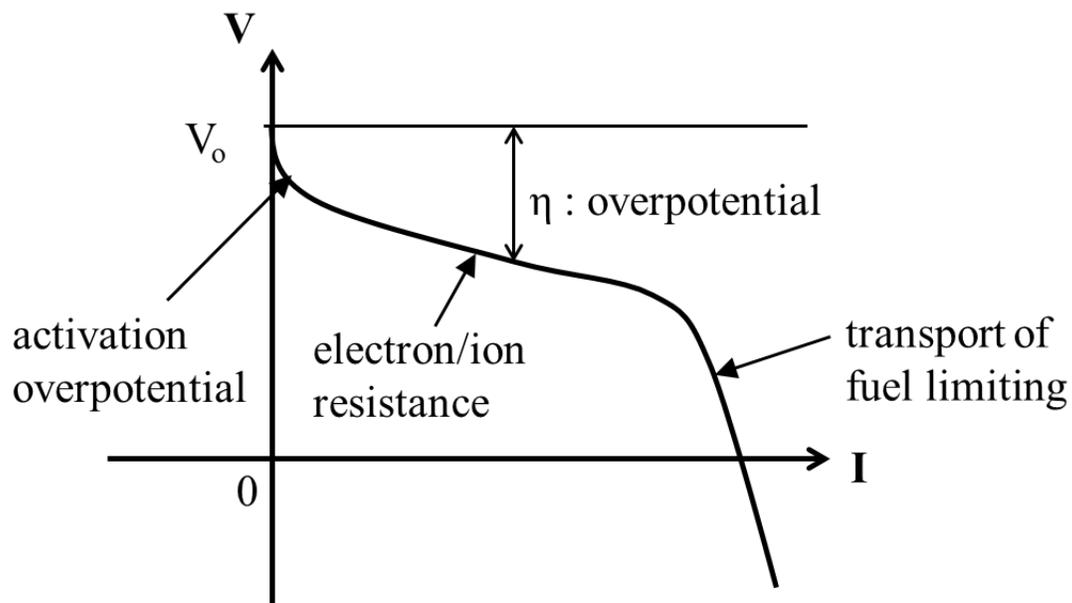


Figure 5. Cell Voltage of Typical Fuel Cells as a Function of Current

MIT OpenCourseWare  
<http://ocw.mit.edu>

10.626 Electrochemical Energy Systems  
Spring 2014

For information about citing these materials or our Terms of Use, visit: <http://ocw.mit.edu/terms>.