1. Introductory Material (Huggins, ch. 1)

1. Chemical & electrochemical reactions
2. Major types of reaction mechanisms
3. Important practical parameters
4. General equivalent circuit of an electrochemical cell

Robert A. Huggins, *Advanced Batteries*, Springer, 2009. (e-book)

1.1 Introduction

-electrochemical storage of energy involves the conversion, or transduction, of chemical energy into electrical energy, and vice versa → electrochemical cells, commonly known as *batteries*

1.2 Simple Chemical and Electrochemical Reactions

$$A+B = AB$$

the standard Gibbs free energies of the reactants

$$\Delta G_r^{o} = \sum \Delta G_f^{o}(products) - \sum \Delta G_f^{\circ}(reactants)$$

If A and B are simple elements, this is called a *formation reaction* → standard Gibbs free energy of formation of elements is zero

$$\Delta G_r^{\circ} = \Delta G_f^{\circ}(AB)$$

-evolution of the microstructure during such a reaction → product phase AB grow (A, B diffuse through AB)

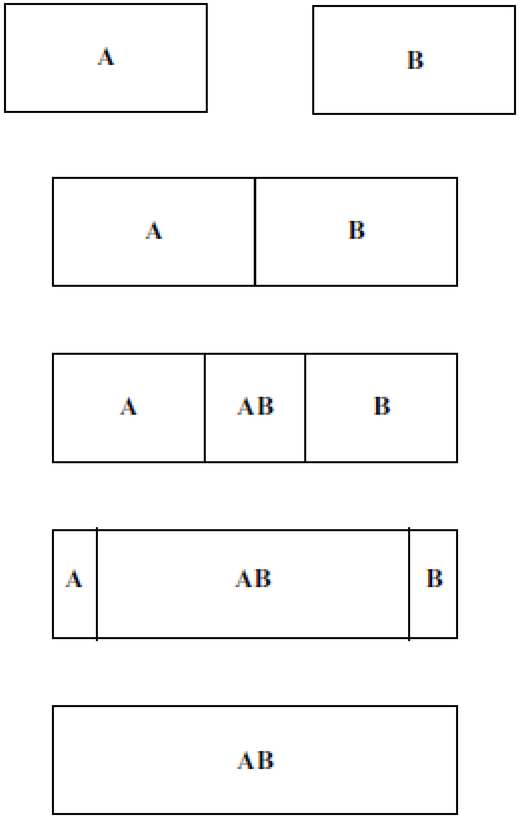

Fig. 1.1 Simple schematic model of chemical reaction of A and B to form AB, indicating how the microstructure of the system varies with time

-process occurs by an *electrochemical mechanism*

(assuming A^+ ions are ionic species in the electrolyte)

$$A = A^+ + e^-$$

$$A^+ + e^- = A$$

$$\Delta G_r^\circ = -zFE$$

ΔG_r° : J/mol

z: charge number of the mobile ionic species

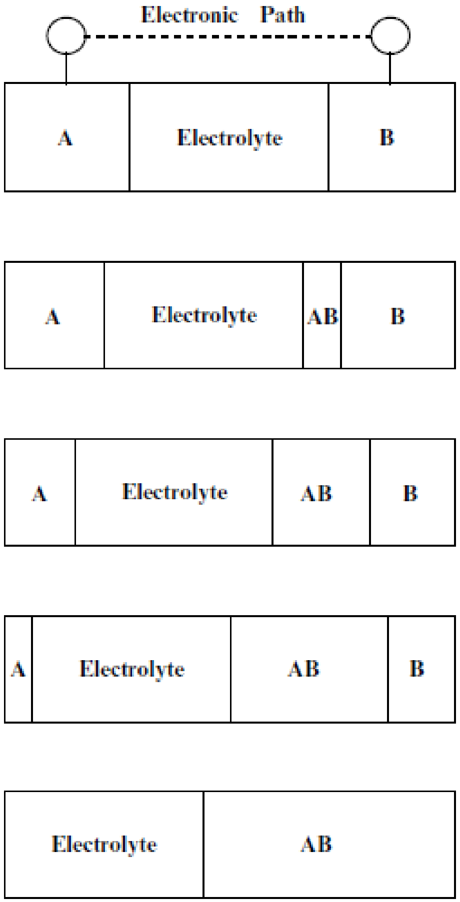

Fig. 1.2 Simple schematic model of time evolution of the microstructure during the electrochemical reaction of *A* and *B* to form *AB*, a mixed conductor. In this case it is assumed that A^+ ions are the predominant ionic species in the electrolyte. To simplify the figure, the external electronic path is shown only at the start of the reaction

1.3 Major Types of Reaction Mechanisms

1.3.1 Reconstitution reactions

-some phases grow and others disappear. The result is that the microstructure of one or more of the electrode materials gets significantly changed, or *reconstituted*.
→ *Phase diagrams* are useful thinking tools to help understand this phenomenon: equilibrium state (thermodynamics)

-Two major types of such reactions: (1) formation reaction (생성반응), (2) displacement reaction (치환반응)

1.3.1.1 Formation Reactions

$$A + B = AB$$

a new phase AB is formed in one of the electrodes from its atomic constituents. This can result from the transport of one of the elements, passing across an electrochemical cell through the electrolyte from one electrode to react with the other component in the other electrode. Since this modifies the microstructure, it represents a reconstitution reaction.

e.g. reaction of lithium with antimony at about 350°C

negative electrode: Li, positive electrode: Sb
Electrolyte: a lithium-conducting molten salt

-equilibrium phase diagram for *lithium - antimony system*

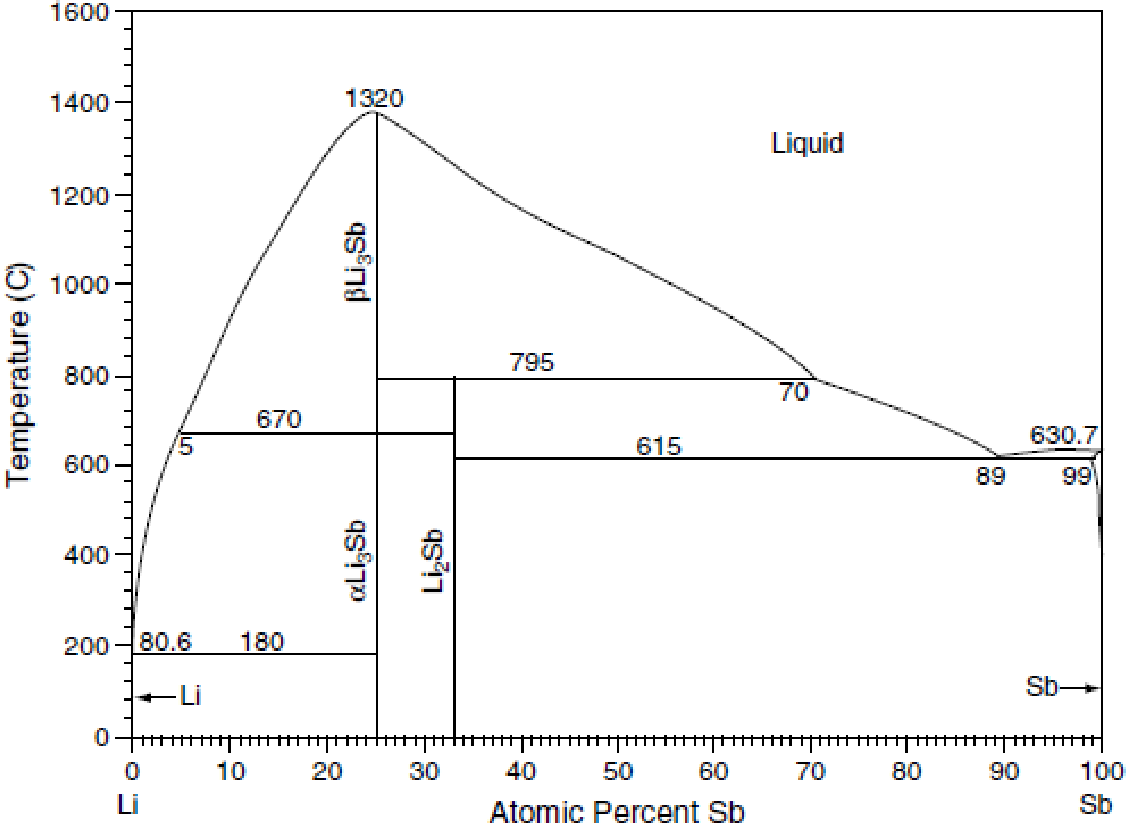

Fig. 1.3 Equilibrium phase diagram of the lithium - antimony system

-Cell voltage is different in different composition

1.3.1.2 Displacement Reactions

Another type of reconstitution reaction involves a *displacement* process

$$A + BX = AX + B$$

-*A* displaces species *B* in the simple binary phase *BX*, forming *AX*.
-A driving force causing this reaction tends to occur if phase *AX* has greater stability, i.e. has a greater negative value of ΔG_f°, than phase *BX*.

-e.g.

$$Li + Cu_2O = Li_2O + Cu$$

-A change in the chemical state in the electrode results in a change in its electrical potential

1.3.2 Insertion reactions

-A quite different reaction mechanism → *insertion* of guest species into unoccupied interstitial sites in the crystal structure of an existing stable host material →
no change in basic crystal structure, or microstructure. however, a change in volume → mechanical stress,
and mechanical energy → insertion and extraction of interstitial species plays a significant role in the hysteresis, and subsequent energy loss

-particular case with layer-type crystal structures, insertion reactions are sometimes called *intercalation* reactions → change in the composition by guest species → "solid solution reaction" (고용체 반응)

-incorporation of such guest species occurs *topotactically*. i.e. guest to be present at specific (low energy) locations, and not randomly distributed.

e.g.

$$xA + BX = A_xBX$$

x amount of species A

$$x\mathrm{Li} + \mathrm{TiS_2} = \mathrm{Li_xTiS_2}$$

-happened in crystalline or amorphous

1.4 Important Practical Parameters

-Specific energy and specific power: energy and power available per unit weight e.g. electric vehicle

-Energy density: the amount of energy that can be stored per unit volume e.g. portable electronics

-Power density: power per unit volume e.g. power tools

-Cycle life: number of times than can be effectively recharged before its performance has become too degraded

-Cost

-Maximum theoretical values → practical system do not achieve these max. theoretical values due to polarizations, less utilization..

-A rule of thumb: practical battery 1/5 ~ ¼ of max. theoretical value

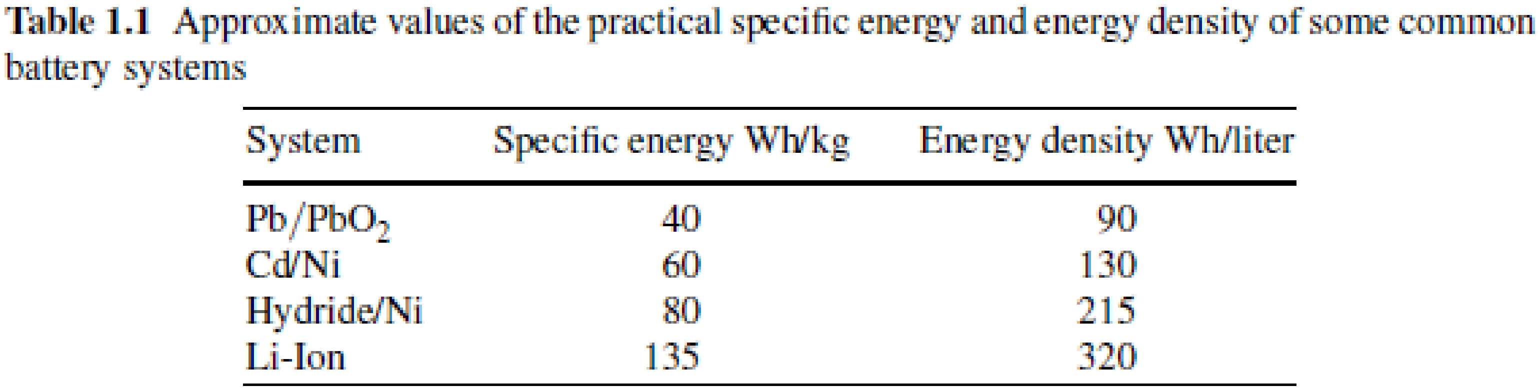

Table 1.1 Approximate values of the practical specific energy and energy density of some common battery systems

System	Specific energy Wh/kg	Energy density Wh/liter
Pb/PbO_2	40	90
Cd/Ni	60	130
Hydride/Ni	80	215
Li-Ion	135	320

-Ragone plot: specific power vs. specific energy

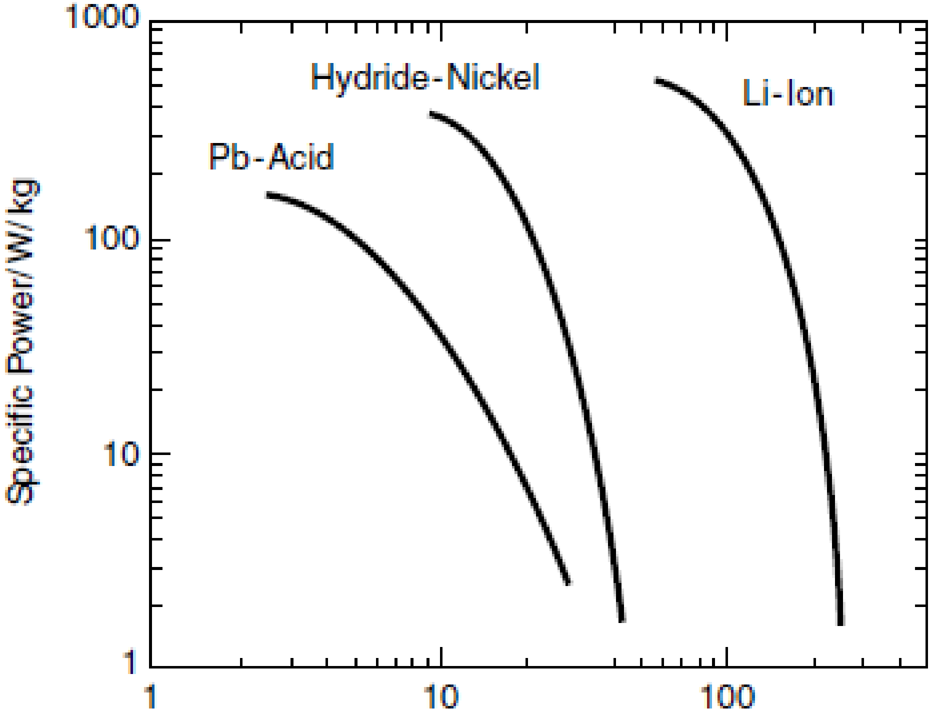

Fig. 1.4 Ragone plot showing approximate practical values of specific power and specific energy of three common battery systems

1.4.1 Operating voltage and energy quality

-Voltage during discharge

-Open circuit voltage (OCV) is determined by the thermodynamics of chemical reaction → actual use, the operating voltage will vary from OCV, depending on various kinetic factors

-Energy quality: analogue concept of heat quality → high T heat is more useful (higher quality) in many applications
→ high voltage energy is often more useful (higher quality) than low voltage energy

e.g. electric power $P = E^2/R$

by square relation → high voltage energy is superior to low voltage stored energy (e.g. light source, electric motor)

-Rough energy quality for electrochemical cell

3.3 ~ 5.5 V	high quality energy
1.5 ~ 3.5 V	medium quality energy
0 ~ 1.5 V	low quality energy

-Electric vehicle (or hybrid) → high voltage required (> 200 V) → individual cell require the highest possible voltage as fewer cells are necessary

-Despite energy quality, matching The requirements of the Applications
e.g. power semiconductor circuit → smaller voltage due to lower the Joule heat output (e.g. computers)

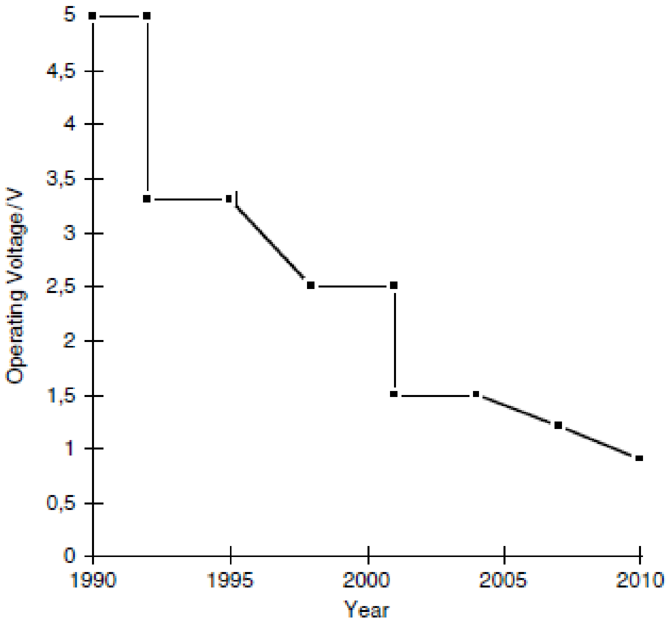

Fig. 1.5 Drop in the required voltage for semiconductor technology since 1990. The last several points indicate predictions for the future

1.4.2 The charge capacity (충전용량)

-Energy is the integral of the voltage x charge capacity

-Charge capacity: the amount of charge available

E: output voltage
q: amount of electric charge (C/mol, C/g, C/ml)

1.4.3 The maximum theoretical specific energy (MTSE)

-Consider an insertion of formation reaction

$$xA + R = A_xR$$

x: number of mols of A that reacts per mol of R
→ is also the number of elementary charges per mol of R

-W_t: sum of molecular weight of reactants

$$\text{MTSE (J/g or kJ/kG)} = (xE/W_t)F$$

x: equivalent per mol, E: volts, W_t: g/mol, F: Faraday const (96500 C/eq)

1 W = 1 J/s, 1 Wh = 3.6 kJ

$$\text{MTSE (Wh/kg)} = 26805\ (xE/W_t)$$

1.4.4 Variation of the voltage as batteries are discharged and recharged

-Discharge curves & charge curves: cell voltage vs. state of charge

-Coulometric titration: V vs. state of charge under equilibrium or near equilibrium conditions

-Charge capacity: the amount of charge available

-Curves: flat, more than one flat, S-shape…

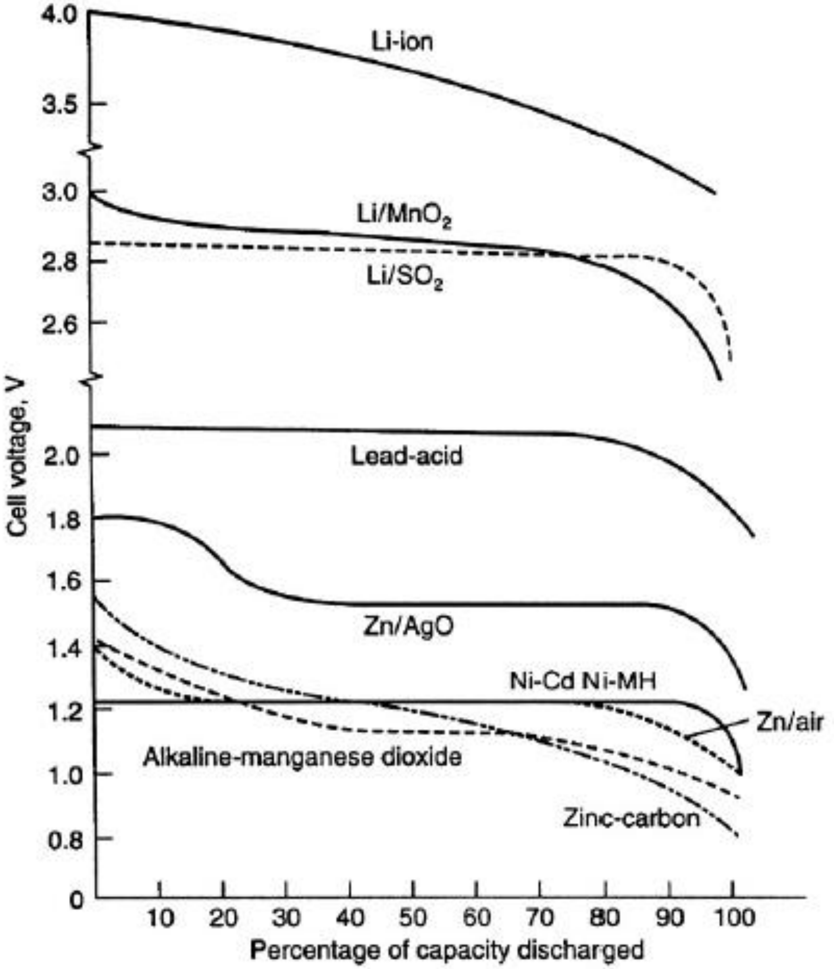

Fig. 1.6 Examples of battery discharge curves, showing variation of the voltage as a function of the fraction of their available capacity

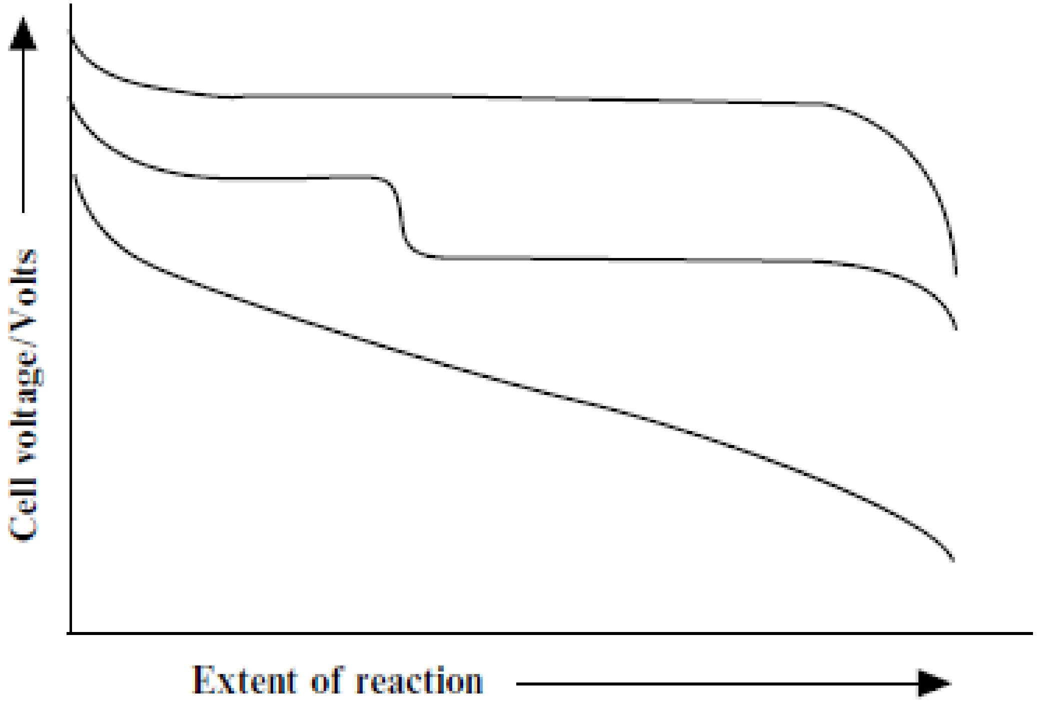

Fig. 1.7 Schematic representation of different types of discharge curves

1.4.5 Cycling behavior (수명특성)

-battery: expected to maintain many discharge-charge cycles

-Coulomb efficiency: fraction of the prior charge capacity that is available during the following discharge

e.g. 99.5% coulomb efficiency → 0.5% loss each cycle → 78% after 50 cycles, 61% after 100 cycles

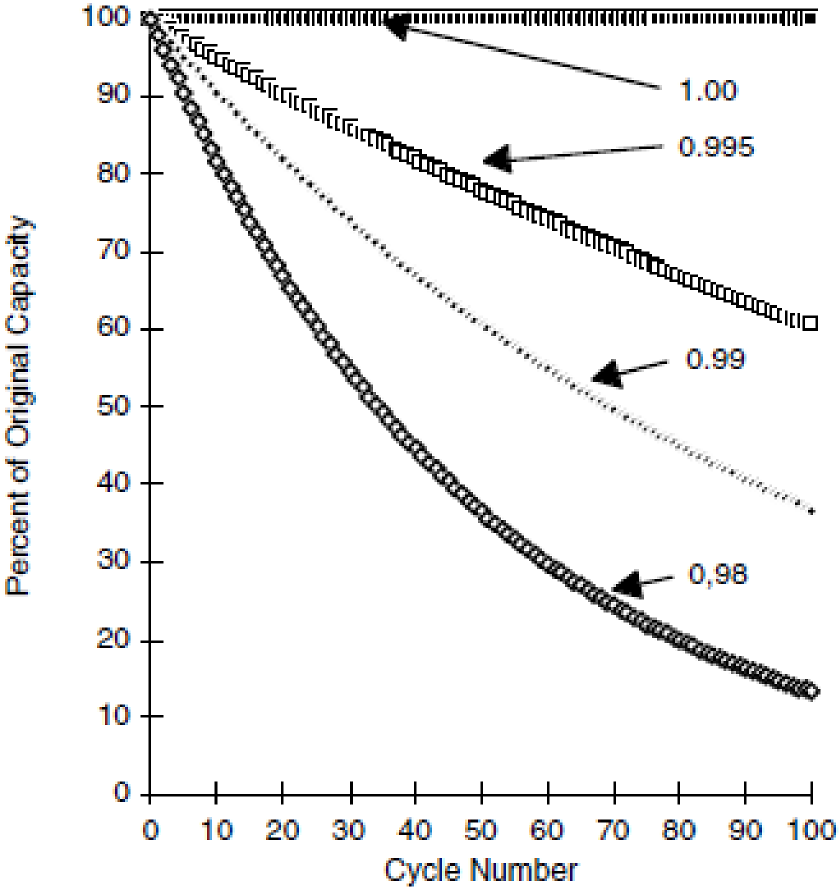

Fig. 1.8 Influence of Coulombic efficiency upon available capacity during cycling

1.4.6 Self-discharge (자가방전)

-decrease in available capacity with time, even without energy being taken from the cell by the passage of current through the external circuit.
-electrochemical self-discharge: transport of charge species
-chemical self-discharge: transport of vapor phase, cracks in electrolyte, dissolved gas in electrolyte

1.5 General equivalent circuit of an electrochemical cell

Theoretical chemical driving force

$$E_{th} = -\Delta G_r^{\circ} / zF$$

If no impedance or other loss, $E_{th} = E_{out}$ (external measurable cell voltage)

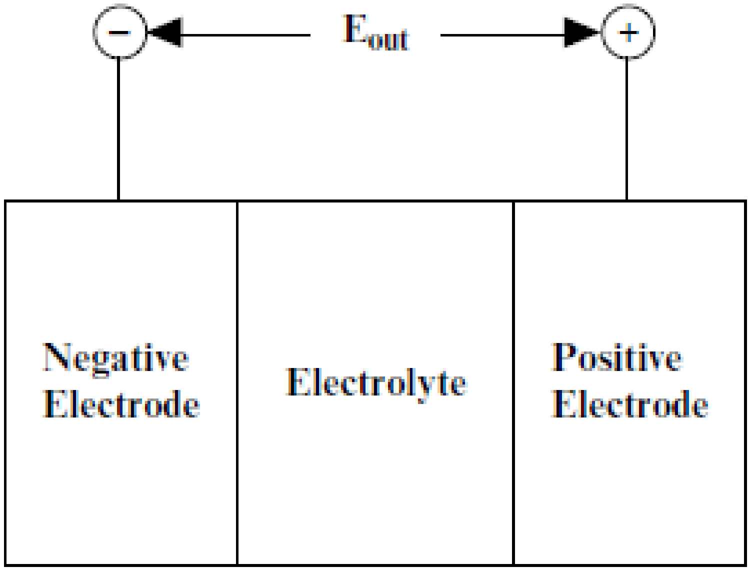

Fig. 1.9 Simplified physical model of electrochemical cell

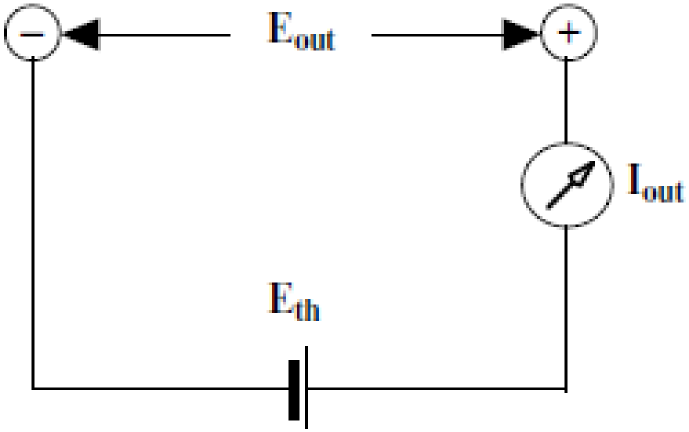

Fig. 1.10 Simple equivalent circuit model of an ideal electrochemical cell

1.5.1 Influence of impedances to the transport of ionic and atomic species within the cell

-Practical cell, $E_{out} \neq E_{th}$

→ impedance to the transport of electroactive ions and related atomic species across the cell

e.g. resistance of electrolyte to ionic transport between two electrolyte/electrode interfaces

-impedance (instead resistance) since can be time-dependent: impedance is instantaneous ratio of the applied force (e.g. voltage) E_{appl} and the response (e.g. current) across any circuit element

e.g. $Z_e = E_{appl} / I_e$

-inverse of impedance: admittance (= ratio, current/voltage)

-under steady state (time-independent) DC conditions, the impwdance and resistance are equivalent

$$E_{out} = E_{th} - I_{out}Z_i$$

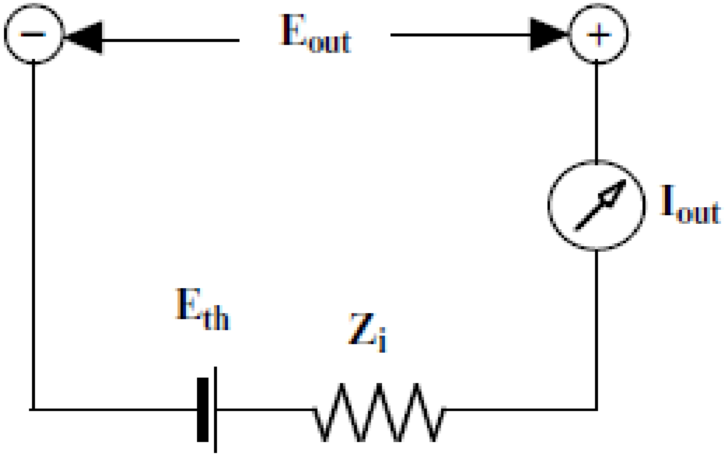

Fig. 1.11 Simple equivalent circuit for a battery or fuel cell indicating the effect of the internal ionic impedance Z_i upon the output voltage

1.5.2 Influence of electronic leakage within the electrolyte

-$E_{out} \neq E_{th}$ even if no external current (I_{out}) flowing → result of electronic leakage through the electrolyte

I_e : transport of electronic species through electrolyte

Parallel, $I_e Z_e = I_i Z_i$

$$E_{out} = E_{th} - I_i Z_i$$

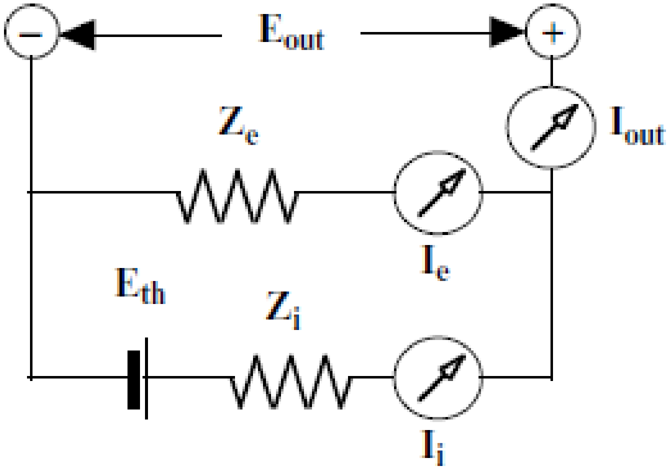

Fig. 1.12 Modified circuit including electronic leakage through the electrolyte

1.5.3 Transference numbers of individual species in an electrochemical cell

-more than one species → relative conductivities or impedances of different species → transference number: the fraction of the total current that passes through the system that is carried by a particular species

e.g. electrons + one type of ions move through the electrochemical cell
Transference number of ions (t_i),
Transference number of electrons (t_e),

-For applied voltage (E_{appl}),

1.5.4 Relations between the output voltage and the values of the ionic and electronic transference numbers

-rearrange Fig. 1.12 → Fig. 1.13

Series combination of Z_i and Z_e acts as a simple voltage divider

If no current passes ou of the system (i.e., under OCV)

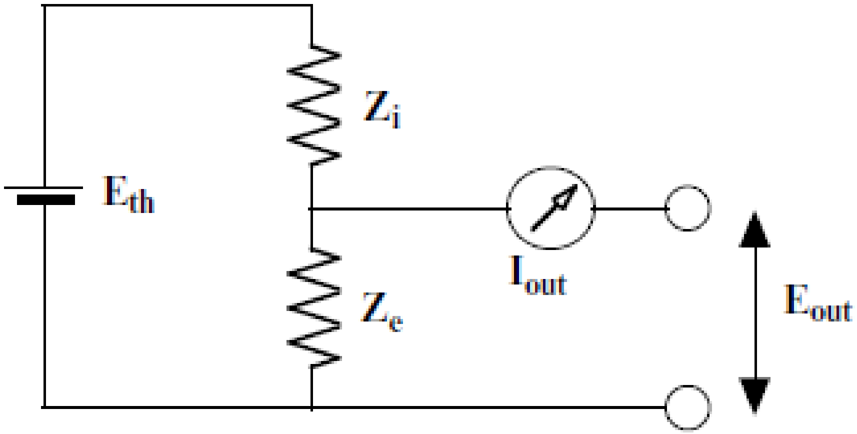

Fig. 1.13 Different representation of general equivalent circuit of Fig. 1.12

1.5.5 Joule heating to due to self-discharge in electrochemical cell

-Electrochemical self-discharge causes heat generation or “Joule heating” due to the transport of charged species through the cell

→ evaluate self-discharge in practical cells

1.5.6 What if current drawn from the cell?

-if no electrochemical self-discharge

I_{out}↑ → discharge curve, Fig. 1.14

“C-rate”: the rate at which a battery is discharged → the discharge rate of a battery is expressed as C/R, where R is the number of hours required to completely discharge its nominal capacity

e.g. battery with a nominal capacity of 5 Ah → discharge at the rate of C/10 would fully discharge it in 10 h → thus the current is 0.5 A. If the discharge rate

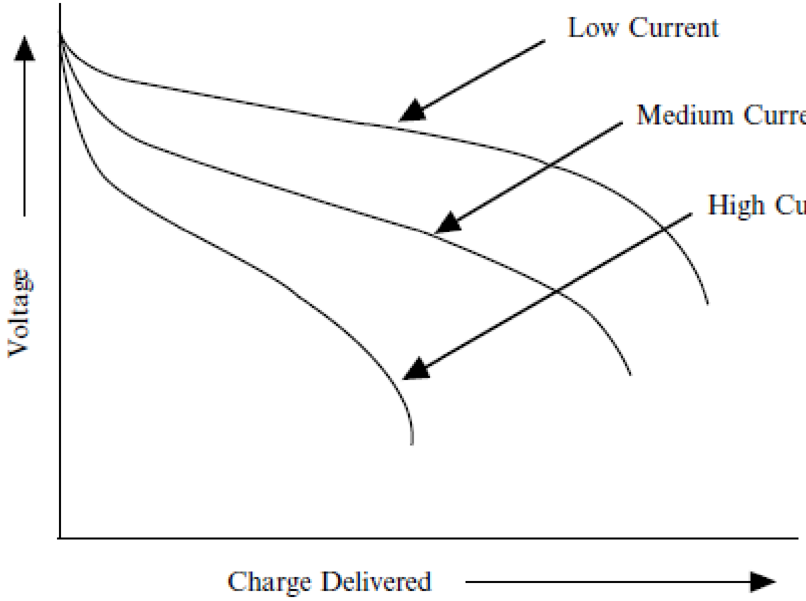

Fig. 1.14 Schematic drawing showing the influence of the current density upon the discharge curve