2019 Fall, 4582-608 (WCU Program) Electrochemical Energy Engineering, 전기화학에너지공학 LECTURER: Professor Yung-Eun Sung (성영은) Office: Rm #729, Phone: 880-1889, E-mail: <u>ysung@snu.ac.kr</u>

OUTLINE

This class deals with electrochemical principles for the electrochemical technologies and energy devices and systems. This course is followed by "Advanced Electrochemistry" in last semester. However, students who did not attend the course in last semester can take this course. After reviewing the basics of electrochemistry, this course will be continued.

TEXTBOOKS

Allen J. Bard, Larry R. Faulkner, *Electrochemical Methods*, Wiley, 2001. (ch. 11–18)

REFERENCES

Heith B. Oldham, Jan C. Myland, Allan M. Bond, *Electrochemical Science & Technology: Fundamentals & Applications*, Wiley, 2013. (e-book, SNU Library)

오승모, 전기화학(3판), 자유아카데미, 2019.



SCHEDULES (will be modified later)

- 1.Basics of electrochemistry (ch. 1 and so on) (1-4 weeks) electrochemistry, I, V, conductivity, Faraday law, Nernst equation, voltammetry, I-V curve (polarization plot), Butler-Volmer equation etc
- 2. Bulk Electrolysis (ch. 11) (5 week)
- 3. Electrode Reactions (ch. 12) (6 week)
- 4. Double Layer Structure and Adsorption (ch. 13) (7-8 weeks)
- 5. Electroactive Layers and Modified Electrodes (ch. 14) (9 week)
- 6. Electrochemical Instrumentation (ch. 15) (10 week)
- 7. Scanning Probe Techniques (ch. 16) (11 week)
- 8. Spectroelectrochemistry (ch. 17) (12-13 weeks)
- 9. Photoelectrochemistry (ch. 18) (14-15 weeks)

GRADING (B⁺ & above ~ 80%, B⁰ & below ~ 20%) Midterm Exam 40%, Final Exam 40%, Homeworks & Attendance 20 %

LECTURE ROOM & TIME: Rm #302-508, 11:00-12:15 Mon. & Wed. **OFFICE HOUR**: Rm #302-729, 13:00-16:00 Mon. & Wed.

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Electrochemical Energy Engineering, 2019

1. Basic concept of electrochemistry

Learning subject

- 1. What is electrochemistry?
- 2. Electrical quantities

Learning objective

- 1. To get information on electrochemistry
- 2. Understanding the definition of electrochemistry
- 3. Understanding electrical quantities

Heith B. Oldham, Jan C. Myland, Allan M. Bond, *Electrochemical Science & Technology: Fundamentals & Applications*, Wiley, 2013. (e-book, SNU Library)

1. What is electrochemistry?

• Electrochemistry: passage of electric current → chemical changes chemical reactions → production of electric energy

• Electrochemistry:

- the coupling of **<u>chemical changes</u>** to the **<u>passage of electricity</u>**
- \rightarrow ionic conduction(flow of ions) + electronic conduction (flow of electrons)
- \rightarrow Electrochemical devices & electrochemical technologies
- \rightarrow Materials & devices & process

Electrochemistry: chemical change ⇔ electric force
Electrodics: in which the reactions at electrodes are considered
Ionics: in which the properties of electrolytes have the central attention → concentration of ions, their mobilities, interactions etc
Basic laws were developed in systems with liquid electrolytes → "solid state" (same and different features of solid electrolyte system)

Ionic solutions

Most important ionic conductor e.g., aqueous solution of electrolyte <u>Electrolyte</u>; a substance that produces ions so enhance the electrical conductivity

e.g., solid(NaCl), liquid(H₂SO₄), gas(NH₃) cf) solid electrolyte

Electrode

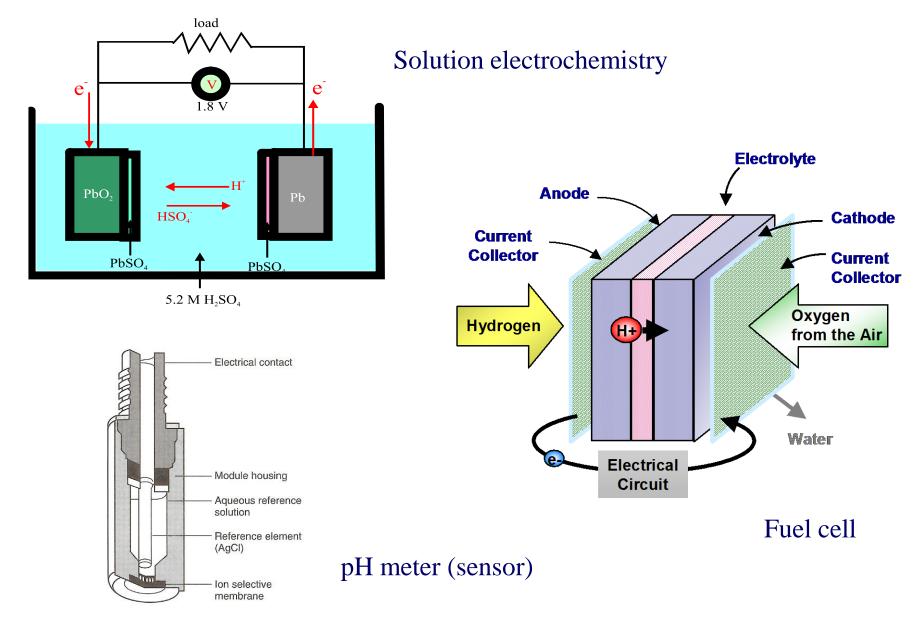
The junction between electronic conductor and ionic conductor that the chemistry of electrochemistry occurs

Electrochemical cell

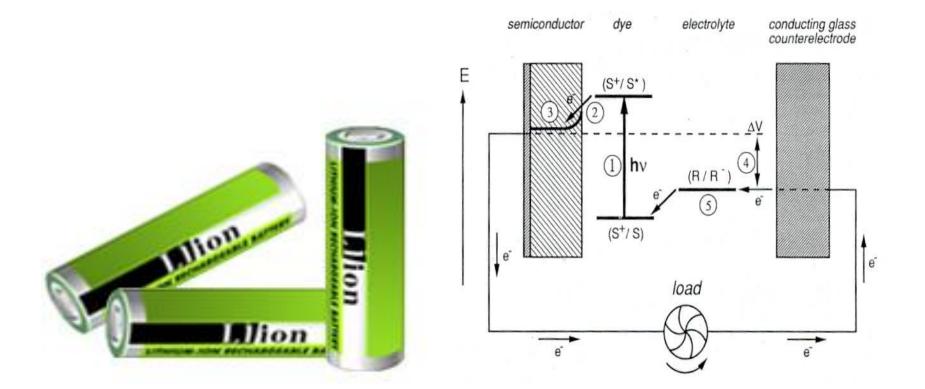
<u>Basic unit</u>: an ionic conductor sandwiched between two electronic conductors e.g., aqueous solution of electrolyte between two pieces of metal, solid electrolyte between two metals

Electronic	lonic conductor	Electronic
conductor	(electrolyte)	conductor
(electrode)		(electrode)

Examples of electrochemical cell 1



Examples of electrochemical cell 2



Dye-sensitized solar cell

Battery

• Examples of Electrochemical devices/technologies

<u>Battery or fuel cell</u>: chemical state changes(electrochemistry) \rightarrow electric power <u>Supercapacitor</u>: double layer phenomena \rightarrow electric power <u>Photoelectrochemical cell</u> (Solar cell): light + electrochemistry \rightarrow electric power <u>Photocatalysis</u>: light \rightarrow hydrogen or chemical reaction <u>Electrochromic display</u>: chemical state changes by electric signal \rightarrow coloration <u>Sensors</u>: chemical state changes by mass \rightarrow electric signal <u>Electrolysis</u>: electric power \rightarrow chemical species by chemical state changes <u>Electrodeposition</u>: electric power \rightarrow chemical change: thin film, Cu metallization <u>Electrochemical synthesis</u>: electric power \rightarrow chemical change <u>Corrosion</u>: potential difference \rightarrow chemical change

Solid State Electrochemistry

<u>Solid electrolyte</u>: solid substances which can conduct electric current by ionic motion as do electrolyte solutions \rightarrow "solid state electrochemistry" or "solid state ionics" \rightarrow "<u>solid state device</u>"

2. Electrical quantities

(1) Electric charge & current

Electric charge (= amount of electricity), q (unit: Coulomb, C), time t Electric current, I (unit: ampere (A)):

I = dq/dt $q = \int Idt$

Current density (unit: A/cm²): i = I/A, A: surface of area

Ammeter: measuring current

Circuit: electric current flows in a closed path

(2) Electrical potential & electric field

Electrical potential (unit; volts, V), ϕ : the pressure of the electric fluid

Voltage: the electrical potential difference $(\Delta \phi)$

Voltmeter: measuring an electrical potential difference

Electric field strength, X (unit: V/m)

 $X = -d\phi/dx$

(3) Ohm's law: most conductors obey this law Current density is proportional to the field strength $i \propto X$

 $i = \kappa X = -\kappa d\phi/dx$

 κ ; electrical conductivity (siemens/m, S = A/V), 1/ κ ; resistivity

 $\Delta \phi = -RI$

R; resistance (unit of ohm), G; conductance,

 $G = 1/R = \kappa A/L = -I/\Delta \phi$

L; conductor length, A; cross section

Ohm's law does not have universal validity. It does not apply to electrochemical cells.

Resistor: a device that is fabricated to have a stable and known resistance

Power (watts) = I^2R

Electrical quantities & their SI units

Quantity	Unit
Current (I)	Ampere (A)
Current density (i)	Ampere per square meter (A/m ²)
Charge (q)	Coulomb ($C = As$)
Charge density (ρ)	Coulomb per cubic meter (C/m ³)
Potential (ϕ)	Volt (V = J/C)
Field strength (X)	Volt per meter (V/m)
Conductivity (κ)	Siemens per meter (S/m)
Resistance (R)	Ohm ($\overline{\Omega} = 1/S = V/A$)
Conductance (G)	Siemens ($S = A/V$)
Permittivity (ε)	Farad per meter ($F/m = C/Vm$)
Energy of work (w)	Joule $(J = VC)$
Power	Watt ($W = J/s = AV$)
Capacitance (C)	Farad (F = $s/\Omega = Ss$), F = C/V

(4) Electrochemical cell potential (V, volts)

1 V = 1 J/C, energy to drive charge between electrodes <u>Electrochemical cell notation</u>:

Zn/Zn²⁺, Cl⁻/AgCl/Ag

Pt/H₂/H⁺, Cl⁻/AgCl/Ag

slash(/): phase boundary, comma(,): two components in the same phase

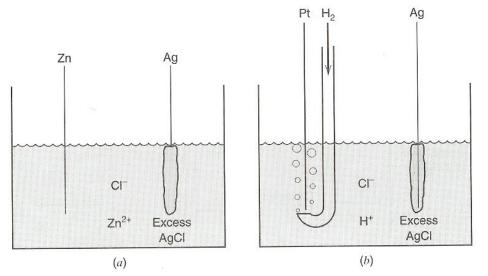


Figure 1.1.1 Typical electrochemical cells. (*a*) Zn metal and Ag wire covered with AgCl immersed in a ZnCl₂ solution. (*b*) Pt wire in a stream of H_2 and Ag wire covered with AgCl in HCl solution.

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001.

(5) energy

Heat: a form of energy

Quantity of heat (Q)

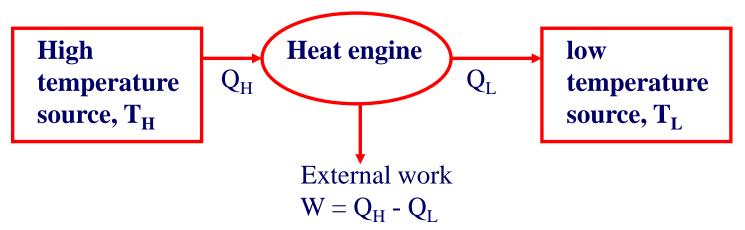
1 calorie: heat to raise 1 g of water through 1° C

1 BTU (British thermal unit): 1 pound (lb) of water through 1 F

Mechanical equivalent of heat

1 cal = 4.186 J 1 BTU = 7718 ft lb = 252 cal = 1054.7 J ~ 0.293 kWh

Ideal heat engine (heat-work converter)



 $Q_H - Q_L = W (1^{st} law of thermodynamics)$ $\eta = work output / work input = W/Q_H = 1 - Q_L/Q_H$

Efficiency

(6) Power

Power: the time rate of doing work or of expending energy

Power = energy/time = work/time

Instantaneous powerP = dW/dtAverage powerP = W/t

Unit: watt (W) = J/s1 horsepower (HP) = 746 W

Power ratings of various devices & animals 10¹⁸ W solar power input to earth 10¹² W electricity capacity in USA (2000) 10⁹ W large electric power plant 10⁷ W train 10⁵ W automobile 1000 W horse 100 W man/woman resting 0.1~1 W Si solar cell 0.01 W human heart e.g., 5933000 BTU = 6259 MJ = 6259 MWs = 6259/3600 MWh (1.739 MWh) 1 kWh = 1000 x 60 x 60 = $3.6 x 10^6$ J ~ 3411 BTU ~ 859.6 Kcal

cf. 1 barrel = 42 US gallons ~ 0.136 tonnes ~ 159 L Fuel equivalence: 1 tonnes oil ~ 1.5 tonnes hard coal ~ 3 tonnes lignite ~ 12000 kWh

Million tonnes of oil equivalent (1 Mtoe = 41.9 PJ) MW(mega-), GW,(giga-) TW(tera-), PW(peta-), EW(exa-): 10^{6} , 10^{9} , 10^{12} , 10^{15} , 10^{18} W

(7) Faraday's law

charge(Q, C(1 C = 6.24 x 10¹⁸ e⁻) vs. extent of chemical reaction "the passage of 96485.4 C causes 1 equivalent of reaction (e.g., consumption of 1 mole of reactant or production of 1 mole of product in a one-electron rxn)" $F = N_A Q_e = (6.02 x 10^{23} mol^{-1})(1.6022 x 10^{-19} C) = 96485 Cmol^{-1}$

- <u>Current (i)</u>: rate of flow of coulombs (or electrons) (1 A = 1 C/s)