Lecture Note #1 (Spring, 2022)

Introduction and basic principles

1. Objectives & syllabus, brief history
2. Electrochemical cells
3. Electrochemical reactions
4. Anode and cathode
5. Electric quantities and units
6. Faraday's law
7. Galvanic cell and electrolytic cell
8. Positive electrode and negative electrode

Fuller & Harb (textbook), ch.1, Pletcher & Walsh (ref.), ch.1, Bard, ch.1, Oh, ch.1

Objectives of the Electrochemical Energy Engineering Lecture
전기화학에너지공학 강의의 목표

- ✓ Cultivation of basic knowledge about electrochemistry.
- ✓ Cultivation of basic knowledge of electrochemical engineering or industrial application.
- ✓ Exploring the applicability of research through the electrochemical reaction of oxidation and reduction.
- ✓ Gain insight into R&D through the history of electrochemistry.
- ✓ Securing synergy by exploring the possibility of joint research with other fields.

- ✓ **전기화학**(Electrochemistry)**에 대한 기초적 지식 함양**
- ✓ **전기화학의 공학 혹은 산업적 응용 기초지식 함양**
- ✓ **산화와 환원의 전기화학반응을 통한 연구에의 적용 가능성 탐색**
- ✓ **전기화학 역사를 통한 연구개발의 통찰력 확보**
- ✓ **타분야와의 공동연구 가능성 모색을 통한 시너지 확보**

Goal: Electrochemistry for Sustainability

Is electrochemistry sustainable in principle?

Google

Is electrochemical energy sustainable?

Electrochemistry for applications in sustainability

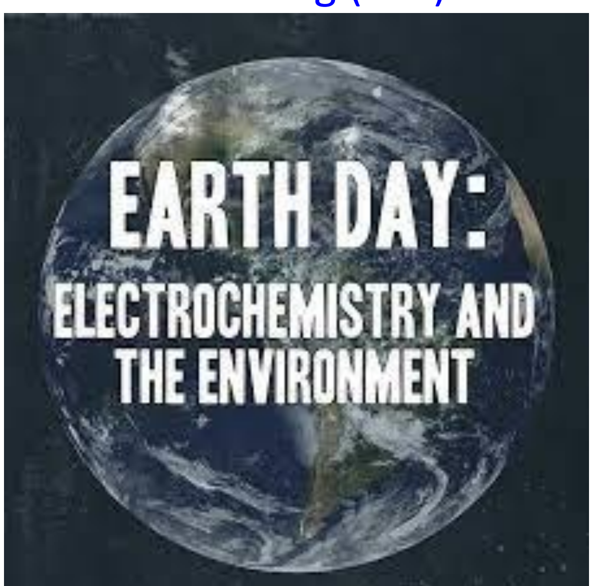
Organic electrochemistry for sustainable synthesis

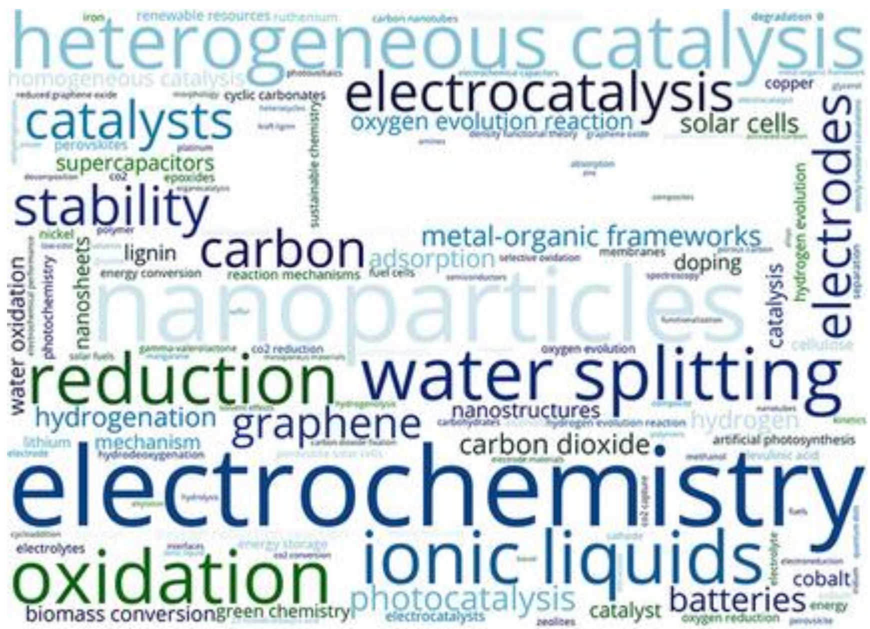
…..

A journey on the electrochemical road to sustainability

(cf. David A. J. Rand, J. Solid State Electrochem., 15 (2011) 1579)

Electrochem.org (ECS)





Davis J. Smith
ChemSusChem
(2019))

Syllabus

2022 Spring, 4582-608 (WCU Program)
Electrochemical Energy Engineering, 전기화학에너지공학
LECTURER: Professor Yung-Eun Sung (**성영은**)
Office: Rm #721 (BLD 302), Phone: 880-1889, E-mail: ysung@snu.ac.kr

OUTLINE

This class deals with electrochemical principles for the industrial electrochemistry, electrochemical engineering and technologies. After reviewing the basics of electrochemistry, this course will be continued to the applications such as electrodeposition, corrosion, electrolysis, battery, fuel cell, photoelectrochemistry, and so on.

전기화학의 기초 원리를 살펴본 다음, 이 원리가 전착, 부식, 수전해, 배터리, 연료전지, 광전기화학, 그리고 기타 전기화학 산업의 이해에 어떻게 적용되는지를 살펴본다. 전기화학 산업을 통해 전기화학을 더 깊이 이해할 필요가 있음을 보고, 또 이를 통해 학생들이 자신의 연구분야에서 응용 가능성을 찾아볼 수 있도록 하려는 것이 이 강의의 목적이다.

TEXTBOOK
Thomas F. Fuller, John N. Harb, Electrochemical Engineering, Wiley, 2018.
(It is recommended to solve the textbook example(Illustration))

REFERENCES (참고문헌들)
Derek Pletcher, Frank C. Walsh, *Industrial Electrochemistry*, Blackie Academic & Professional, 1993.
오승모, 전기화학(3판), 자유아카데미, 2019. (Seung Mo Oh, Electrochemistry, Eng. Version)
Milan Paunovic, Mordechay Schlesinger, *Fundamentals of Electrochemical Deposition*, Wiley, 1998.
Denny A. Jones, *Principles and Prevention of Corrosion*, Macmillan, 1992.
Mathew M. Mench, *Fuel Cell Engines*, Wiley, 2008.
Robert A. Huggins, *Advanced Batteries*, Springer, 2009. (e-book in library, also in Korean)
Allen J. Bard, Larry R. Faulkner, *Electrochemical Methods*, Wiley, 2001 (Korean Ver.)

GRADING **(B^+ & above ~ 80%, B^0 & below ~ 20%, or Departmental guide)**
Midterm Exam 40%, Final Exam 40%, Homeworks & Attendance 20 %

LECTURE ROOM & TIME: Rm #302-409, 11:00-12:15 Mon. & Wed.
OFFICE HOUR: Rm #302-721, 13:00-16:00 Mon. & Wed.
•**TA**: Geumbi Na(**나금비**) Rm #302-1007, 02-880-9123, mstu2025@snu.ac.kr

SCHEDULES (could be modified)

- Introduction and basic principles (ch.1) (1 week)
- Cell potential and thermodynamics (ch.2) (2 week)
- Electrochemical kinetics (ch.3) (3 week)
- Transport (ch.4) (4 week)
- Electrode structures and configurations (ch.5) (5 week)
- Analysis of electrochemical systems (ch.6) (6 week)
- Batteries 1, 2 (ch.7,8) (7,8 weeks)
- Fuel cells 1, 2 (ch.9,10) (9,10 weeks)
- Electrochemical capacitors (ch.11) (11 week)
- Energy storage & conversion (ch.12) (11 week)
- Electrodeposition (ch.13) (12 week)
- Industrial electrolysis (ch.14) (13 week)
- Photoelectrochemical cells (ch.15) (14 week)
- Corrosion (ch.16) (15 week)

*Due to COVID-19, lecture will be held online Zoom in March. However, I am going to give a lecture in Lecture Room 409 and I will stay there until 1 pm, so if you have any questions, please come to the classroom or use online zoom after class.

Electrochemistry (전기화학)

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

coupling of chemical changes to the passage of electricity
→ electron + ion conduction (flow of electrons & ions)
→ Electrochemical devices & technologies
→ Materials & devices & process

Electrochemical reaction:
Oxidation or/and reduction reactions involving electrons

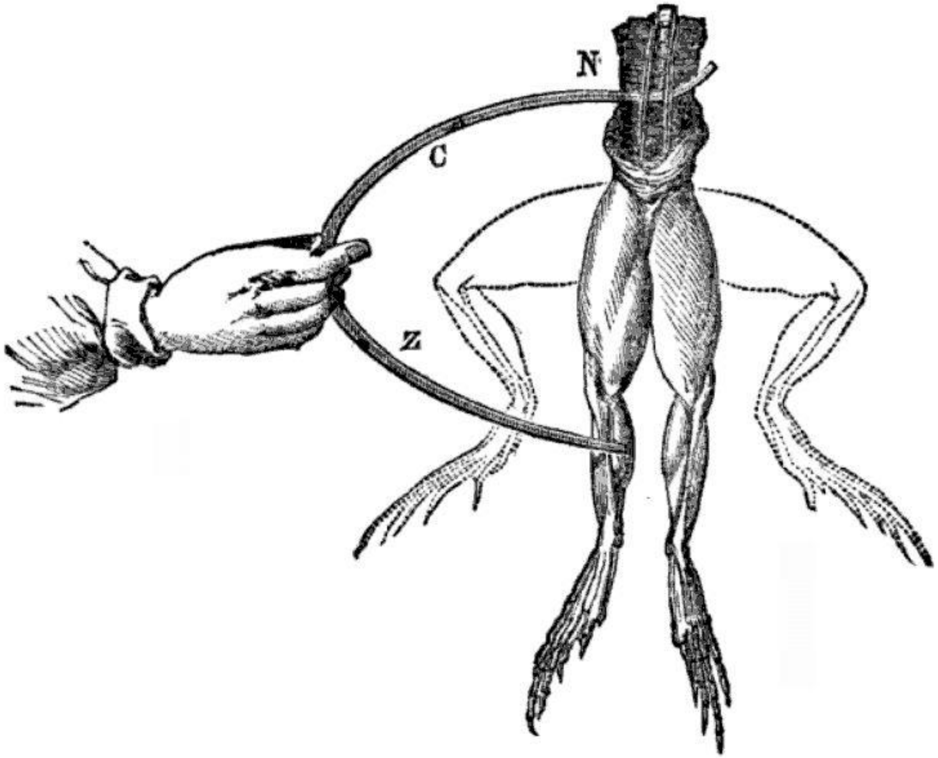
Examples

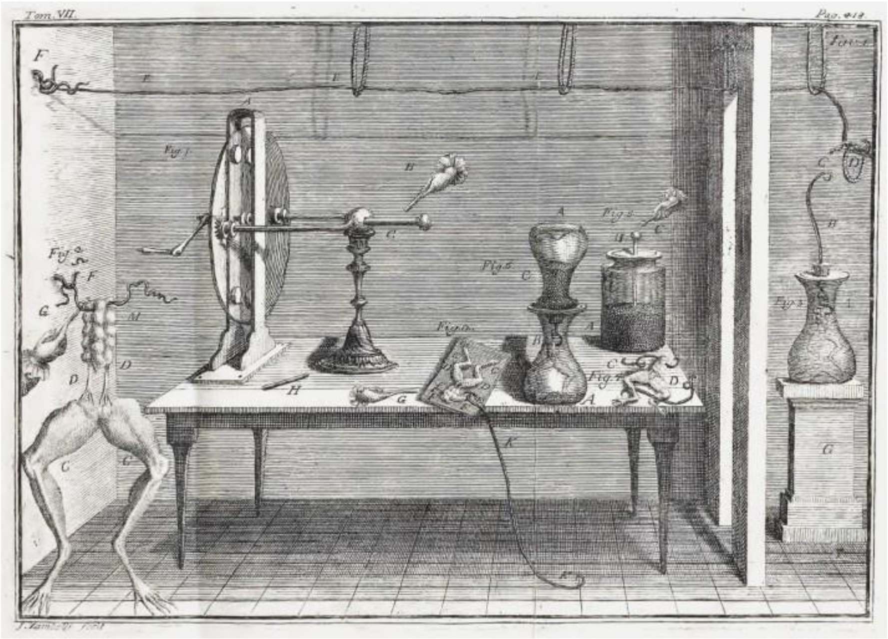
- ✓ Battery or fuel cell: chemical state changes → electric power
- ✓ Supercapacitor: double layer phenomena → electric power
- ✓ Photoelectrochemical cell (Solar cell): photoelectrochemistry → power
- ✓ Photocatalysis: light → hydrogen or chemical reaction
- ✓ Electrochromic: chemical state changes by electric signal → coloration
- ✓ Sensors: chemical state changes by mass → electric signal
- ✓ Electrolyzer: electric power → chemical species
- ✓ Electrodeposition: electric power → thin film, Cu metallization
- ✓ Electrochemical synthesis: electric power → chemical change
- ✓ Corrosion: potential difference → chemical change
- ✓ Etching & Surface treatment
- ✓ Bioelectrochemistry
- ✓ Environmental electrochemistry

History of electrochemistry

- ✓ Thales(탈레스, ~BC 600): Rubbing amber (호박, mineral) with fur pulls feathers
  "Some of the objects in nature are alive with immortal souls."
- ✓ Aristotle(아리스토텔레스): Electric(?) Stingrays(가오리) have the ability to stun prey
- ✓ ~1600 William Gilbert(길버트): From the Greek electron (ηλεκτρον) for amber(호박), the words 'electric' and 'electrica' were made. There is positive and negative electricity
- ✓ 1785 Coulomb(쿨롱) Coulomb's law discovered from attraction of positive & negative charges
- ✓ 1791 Galvani(갈바니): Discharge causes frog legs to move
- ✓ 1800 Volta(볼타): electricity generator (battery, 전지)
- ✓ Humphrey Davy, 데이비 1778-1829): Proposed oxygen generating electrode as positive and hydrogen generating electrode as negative during electrolysis of water
  → positively charged hydrogen ions move to the negative
  물의 전기분해시 산소발생 전극을 양극(positive), 수소발생 전극을 음극(negative)으로 제안 → 양의 전하를 띤 수소이온이 음극으로 이동
- ✓ Michael Faraday, 패러데이 1791-1867) "Current is the movement of a positive charge from a positive electrode to a negative electrode" definition. Faraday law
  "전류는 양의 전하가 양의 전극에서 음의 전극으로 이동하는 것이다" 정의, 전기분해 법칙
- ✓ 1897 Thomson(톰슨) electron discovery→ The direction in which electrons flow is opposite to the direction in which current flows. 전자가 흐르는 방향이 전류가 흐르는 방향의 반대이다

Galvani experiment (History)

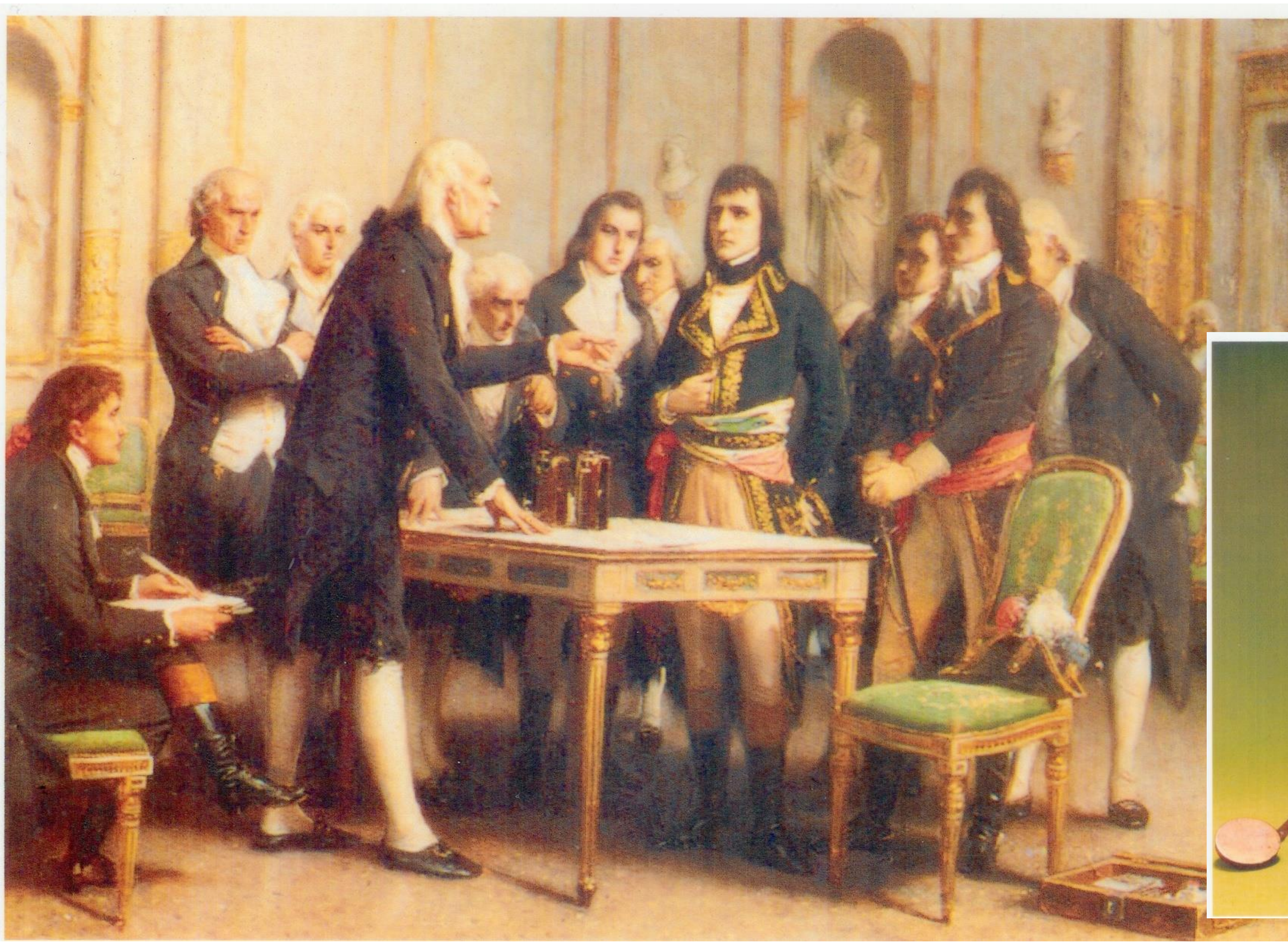


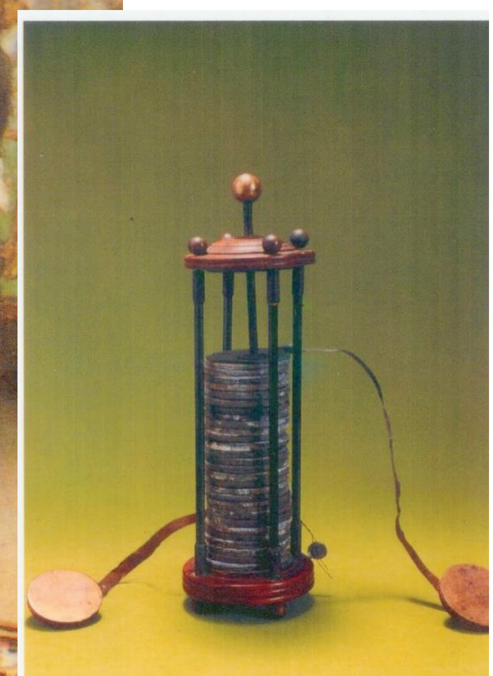


Frog leg experiment
개구리 뒷다리 실험

Galvanic cell
Pacemaker(심장박동기)

Volta battery (History)





Volta

battery

voltage, volt (V)

Volta paper (History)

XVII. *On the Electricity excited by the mere Contact of conducting Substances of different kinds. In a Letter from Mr.* Alexander Volta, *F. R. S. Professor of Natural Philosophy in the University of Pavia, to the Rt. Hon. Sir* Joseph Banks, *Bart. K. B. P. R. S.*

Read June 26, 1800.

A Côme en Milanois, ce 20me Mars, 1800.

Après un long silence, dont je ne chercherai pas à m'excuser, j'ai le plaisir de vous communiquer, Monsieur, et par votre moyen à la Société Royale, quelques resultats frappants auxquels je suis arrivé, en poursuivant mes expériences sur l'électricité excitée par le simplé contact mutuel des métaux de différente espèce, et même par celui des autres conducteurs, aussi différents entr'éux, soit liquides, soit contenant quelque humeur, à laquelle ils doivent proprement leur pouvoir conducteur. Le principal de ces resultats, et qui comprend à-peu-près tous les autres, est la construction d'un appareil qui ressemble pour les effets, c'est-à-dire, pour les commotions qu'il est capable de faire éprouver dans les bras, &c. aux bouteilles de Leyde, et mieux encore aux batteries électriques foiblement chargées, qui agiroient cependant sans cesse, ou dont la charge, après chaque explosion, se rétabliroit d'elle-même; qui jouiroit, en un mot, d'une charge indéfectible, d'une action sur le fluide électrique, ou impulsion, essentiellement, et

From: *Philosophical Transactions, of the Royal Society of London*. For the Year MDCCC. Part I. London, printed by W. Bulmer and Co. Cleveland-row, St. James's; and sold by Peter Elmsly, Printer to the Royal Society. MDCCC, pp. 403-431.

THE

PHILOSOPHICAL MAGAZINE.

SEPTEMBER 1800.

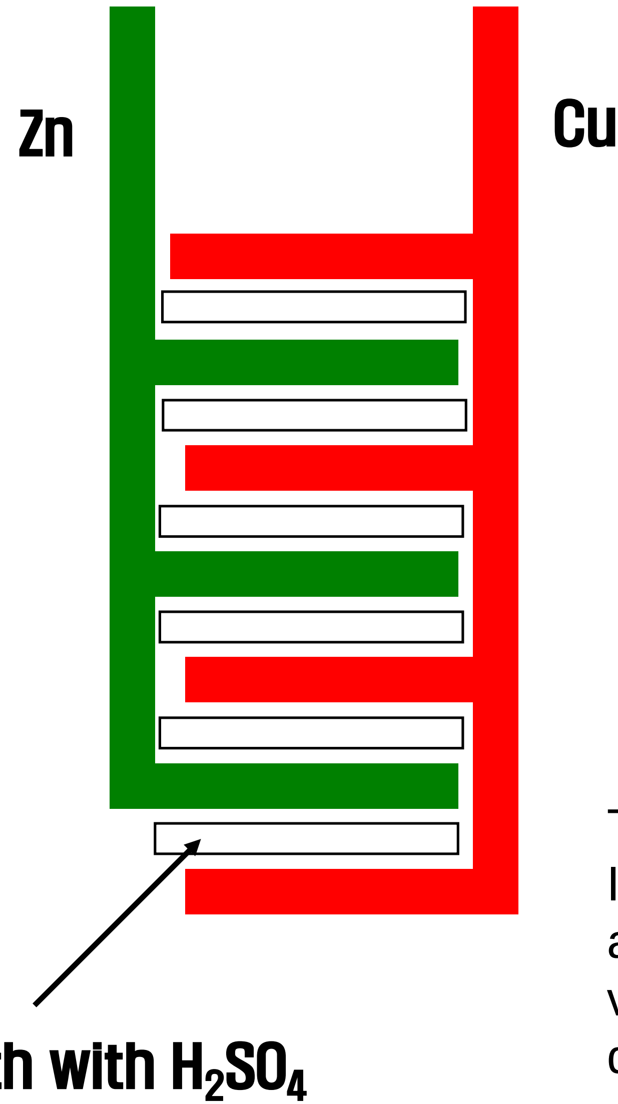
I. *On the Electricity excited by the mere Contact of conducting Substances of different Kinds. In a Letter from Mr.* Alexander Volta, *F.R.S. Professor of Natural Philosophy in the University of Pavia, to the Right Hon. Sir* Joseph Banks, *Bart. K. B. P. R. S.**

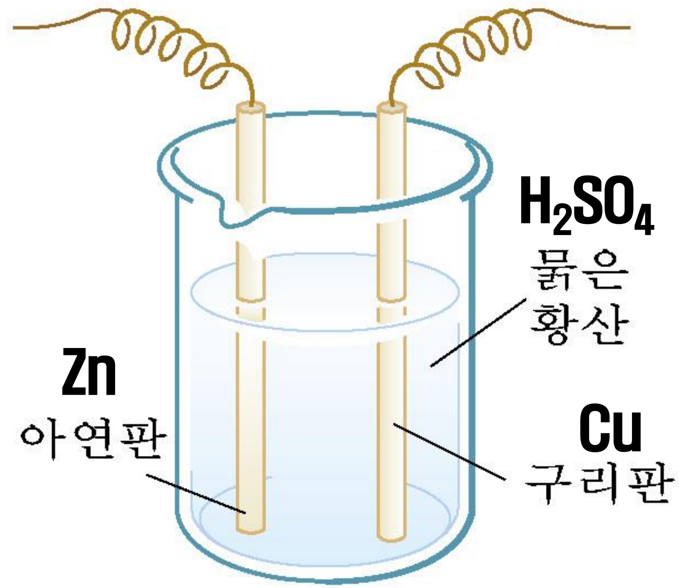
Como in the Milanese, March 20, 1800.

After a long silence, for which I shall offer no apology, I have the pleasure of communicating to you, and through you to the Royal Society, some striking results I have obtained in pursuing my experiments on electricity excited by the mere mutual contact of different kinds of metal, and even by that of other conductors, also different from each other, either liquid or containing some liquid, to which they are properly indebted for their conducting power. The principal of these results, which comprehends nearly all the rest, is the construction of an apparatus having a resemblance in its effects (that is to say, in the shock it is capable of making the arms, &c. experience) to the Leyden flask, or, rather, to an electric battery weakly charged acting incessantly, which should charge itself after each explosion; and, in a word, which should have an inexhaustible charge, a perpetual action or impulse on the electric fluid; but which differs from it essentially both by this continual action, which is peculiar to

* Translated from the author's paper published in French in the Philosophical Transactions for 1800, part 2.

Volta battery (1800)





✓ **oxidation : $Zn \rightarrow Zn^{2+} + 2e^-$**

✓ **reduction : $2H^+ + 2e^- \rightarrow H_2$**

The battery was invented in 1800 by Volta in Italy. Copper as the cathode, zinc as the anode, and sulfuric acid solution as the electrolyte. The voltage is about 1.1V. At the anode, zinc dissolved, and at the cathode, hydrogen ions are reduced to generate hydrogen gas.

Oxidation and reduction

Indicate in the following reactions which are reductions and which are oxidations:

(1) $Fe^{2+} + 2e^- \rightarrow Fe$ (2) $Cl^- \rightarrow 1/2Cl_2 + e^-$ (3) $Fe^{2+} \rightarrow Fe^{3+} + e^-$

(4) $CrO_4^{2-} + 3e^- \rightarrow Cr^{3+}$ (5) $O_2 + 4e^- \rightarrow 2O^{2-}$ (6) $Br_2 + 2e^- \rightarrow 2Br^-$

Basic concepts of electrochemistry

- An electrochemical reaction is a heterogeneous chemical process involving the transfer of charge to or from an electrode, generally a metal, carbon or a semiconductor

- Cathodic process: reduction by the transfer of electrons from an electrode (cathode, 환원극, 환원전극)

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

$$Na^+ + e^- + Hg \longrightarrow NaHg$$

$$2CH_2 = CHCN + 2H_2O + 2e^- \longrightarrow (CH_2CH_2CN)_2 + 2OH^-$$

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$$

- Anodic process: oxidation by the removal of electrons to the electrode

$$2H_2O - 4e^- \longrightarrow O_2 + 4H^+$$

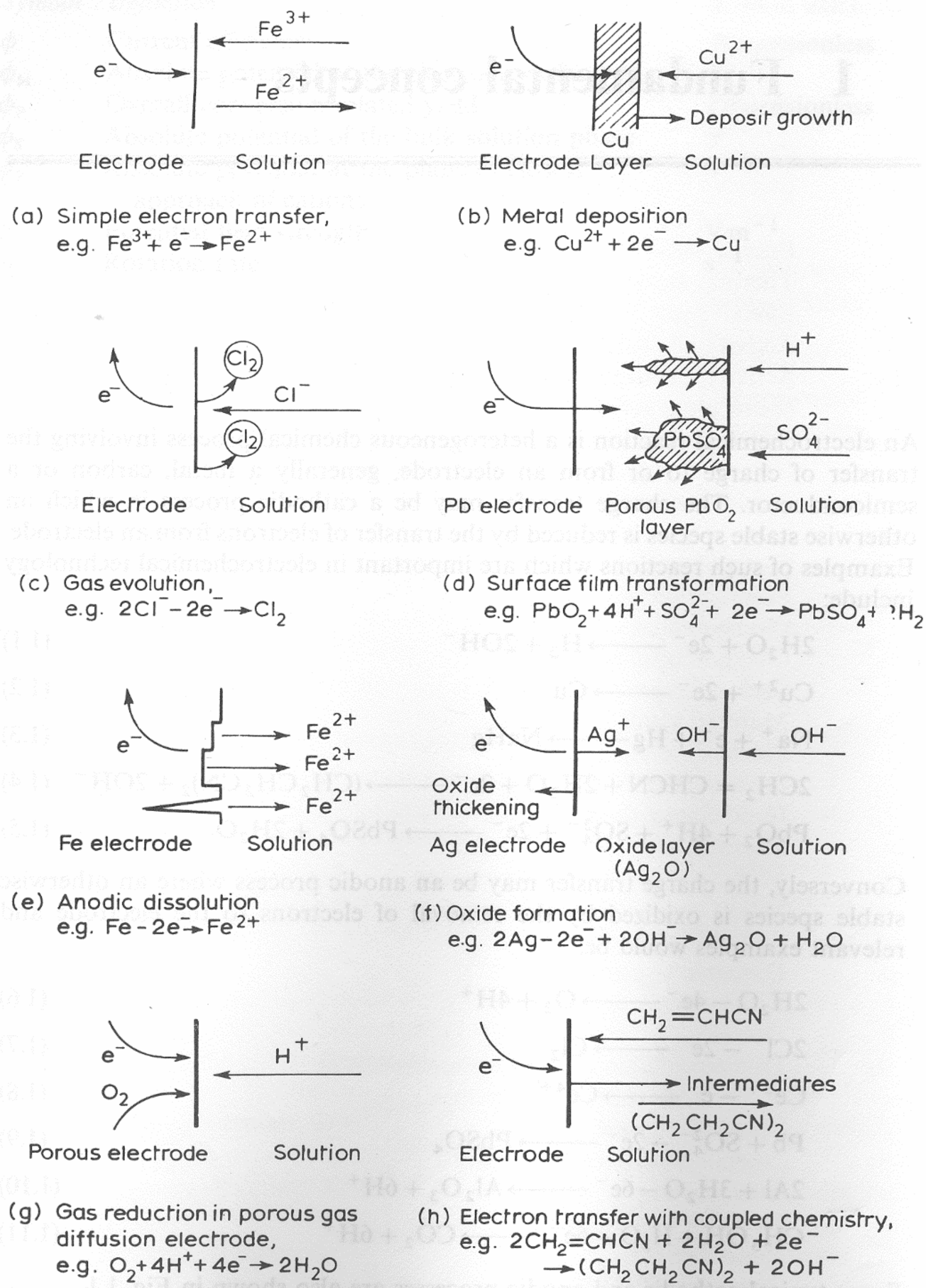
$$2Cl^- - 2e^- \longrightarrow Cl_2$$

$$Ce^{3+} - e^- \longrightarrow Ce^{4+}$$

$$Pb + SO_4^{2-} - 2e^- \longrightarrow PbSO_4$$

$$2Al + 3H_2O - 6e^- \longrightarrow Al_2O_3 + 6H^+$$

$$CH_3OH + H_2O - 6e^- \longrightarrow CO_2 + 6H^+$$



(a) Simple electron transfer, e.g. $Fe^{3+} + e^- \rightarrow Fe^{2+}$

(b) Metal deposition e.g. $Cu^{2+} + 2e^- \rightarrow Cu$

(c) Gas evolution, e.g. $2Cl^- - 2e^- \rightarrow Cl_2$

(d) Surface film transformation e.g. $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2$

(e) Anodic dissolution e.g. $Fe - 2e^- \rightarrow Fe^{2+}$

(f) Oxide formation e.g. $2Ag - 2e^- + 2OH^- \rightarrow Ag_2O + H_2O$

(g) Gas reduction in porous gas diffusion electrode, e.g. $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

(h) Electron transfer with coupled chemistry, e.g. $2CH_2{=}CHCN + 2H_2O + 2e^- \rightarrow (CH_2CH_2CN)_2 + 2OH^-$

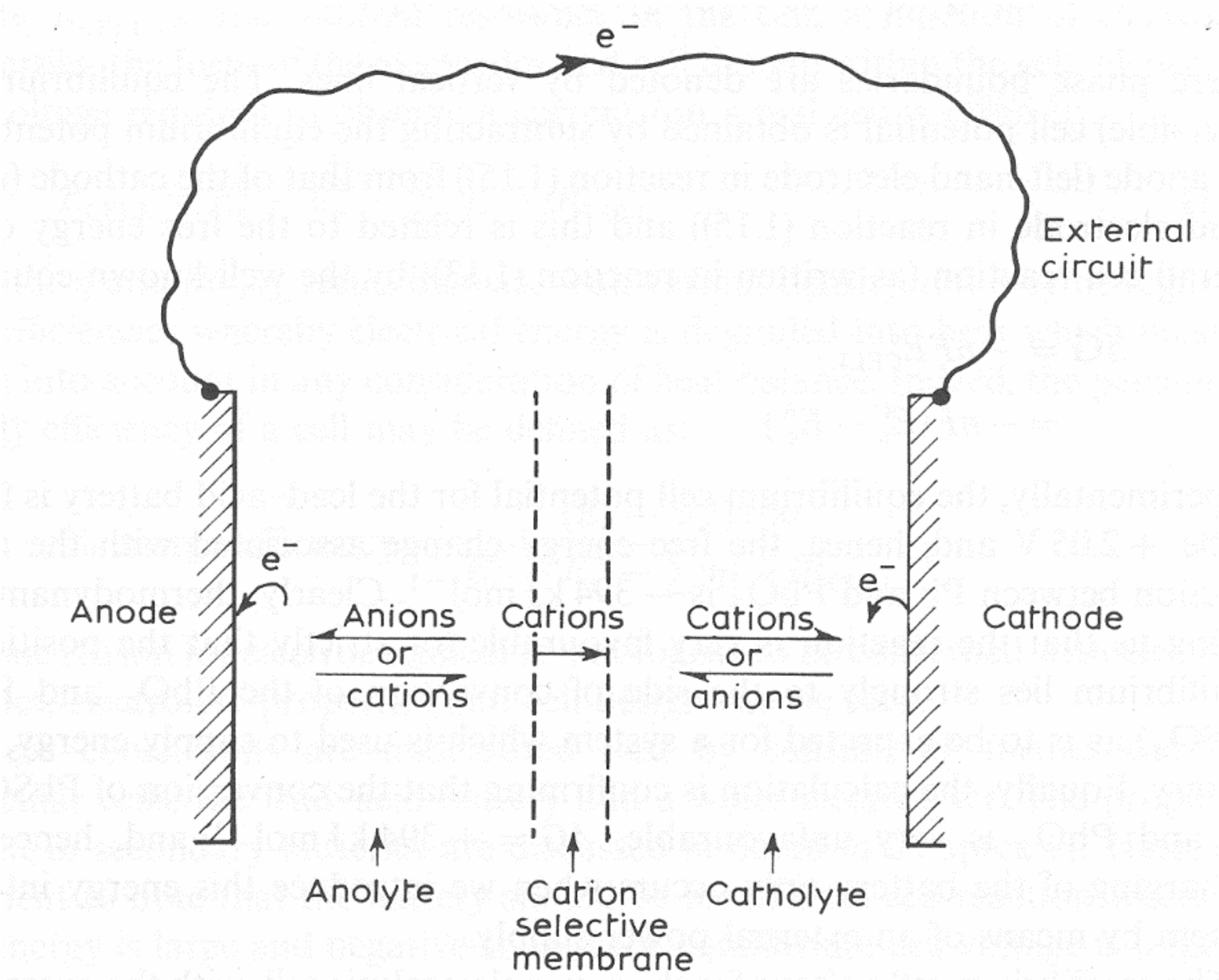
Illustration 1.1

It is strongly recommended to solve the textbook example (Illustration)!!

Pletcher, Fig.1.1

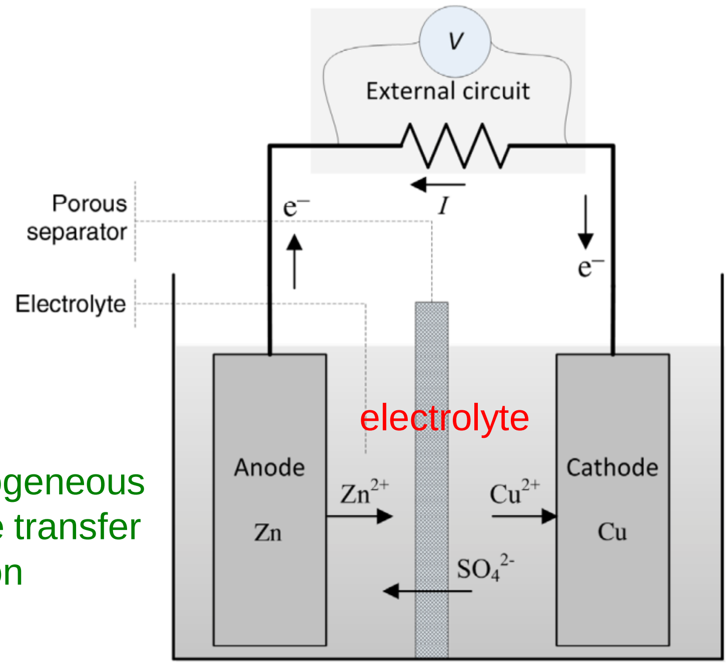
Electrochemical cell

- Electrochemical cell : contains anode and cathode, the amount of reduction at the cathode and oxidation at the anode must be equal



Pletcher, Fig.1.2

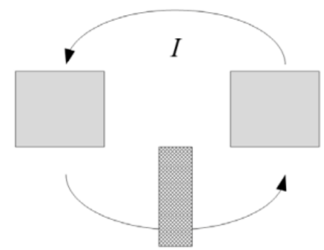
- Daniel cell (1836): contains anode and cathode, the amount of reduction at the cathode and oxidation at the anode must be equal



Heterogeneous charge transfer reaction

Half-cell reaction $Zn \rightarrow Zn^{2+} + 2e^-$ $Cu^{2+} + 2e^- \rightarrow Cu$

anode cathode

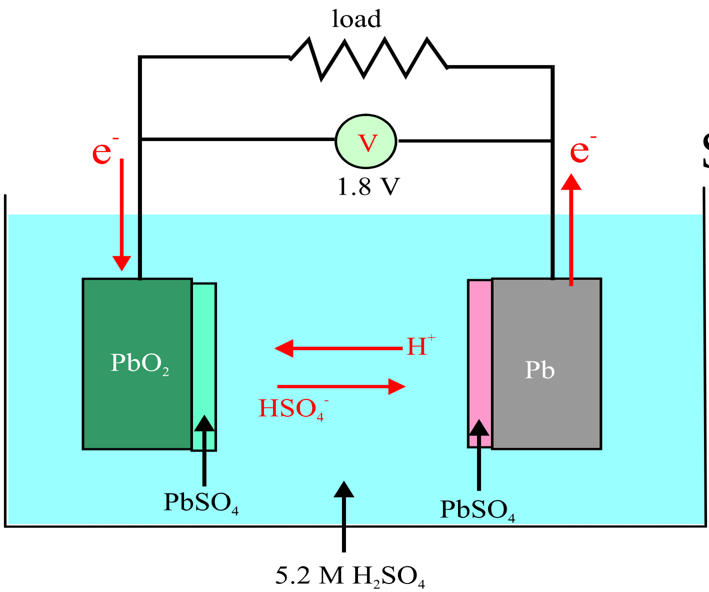


$$\sum I = 0$$

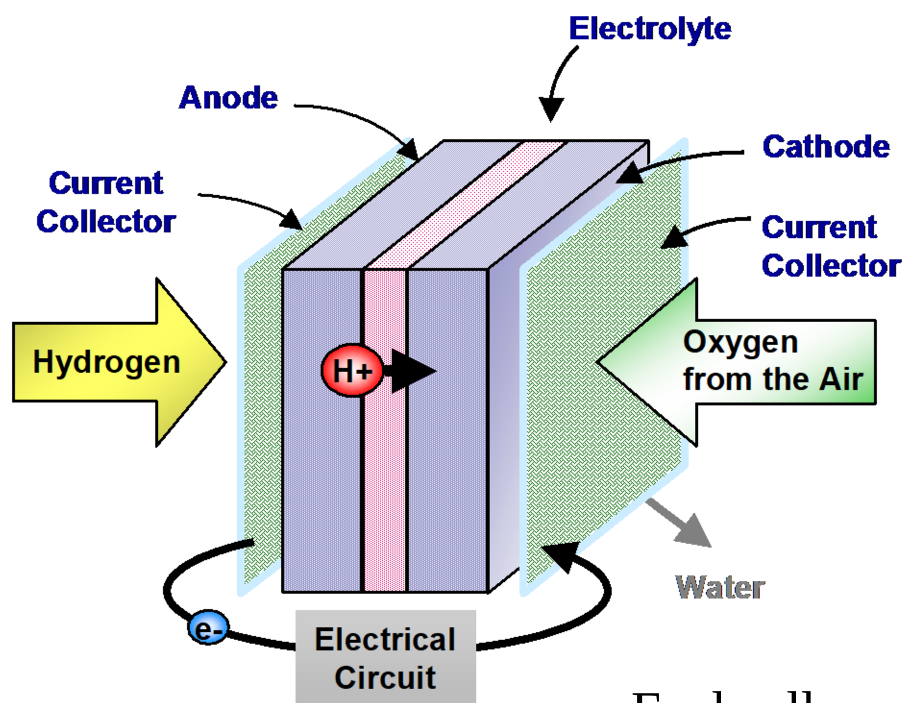
Figure 1.1 A Daniell cell is an example of an electrochemical cell. During steady operation, a constant current flows throughout the cell. For any given volume, the current entering and leaving must sum to zero since charge is conserved.

Full-cell reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

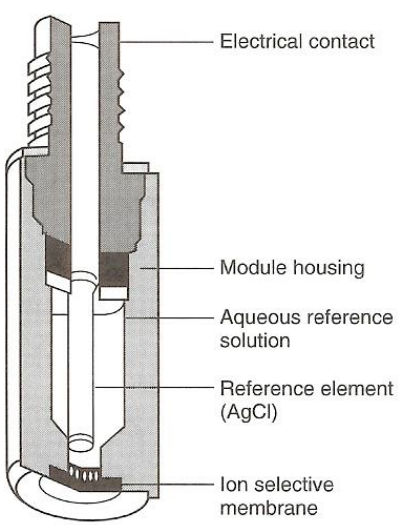
Electrochemical Cell



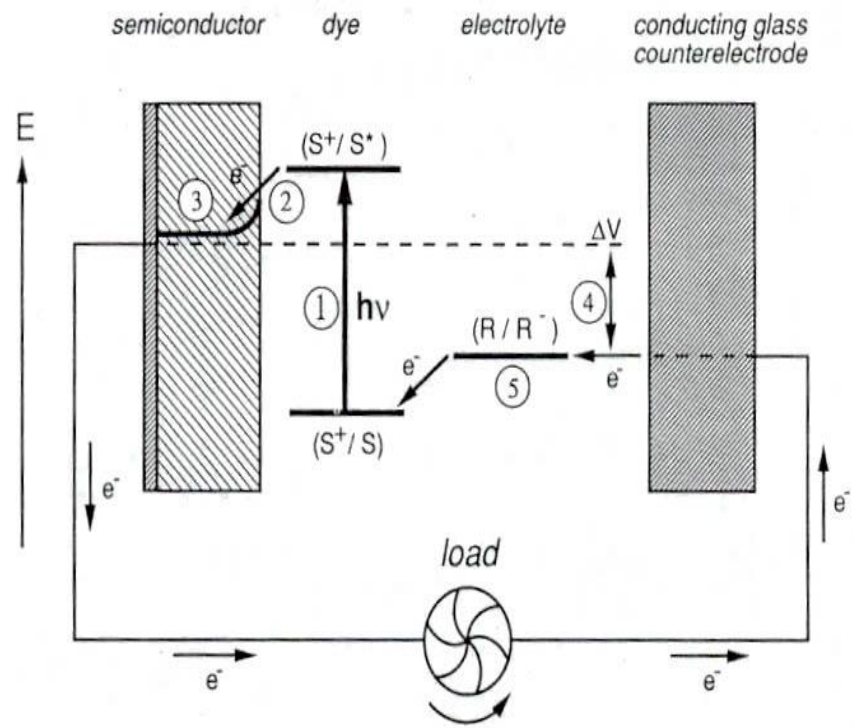
Solution electrochemistry



Fuel cell



pH meter (sensor)



Battery

Photoelectrochemical cell
(dye-sensitized solar cell)

Characteristics of electrochemical reactions

- Separation of the oxidation (anodic) and reduction (cathodic) reactions
- Use of electrons to perform work
- Direct measurement of reaction rates by measuring electric current
- Control of the direction and rate of reaction

Oh, ch.1

- Electrode potential is a representation of the electron energy present inside the electrode
- Electrochemical reactions are possible only near the electrode surface
- The electrochemical reaction proceeds through several steps.
- Current is an expression of reaction rate
- Current flows in a closed loop within the electrochemical cell
- If charge transfer determines the overall rate, the magnitude of the current can be controlled by changing the electrode potential.
- Electrode potential and current cannot be adjusted at the same time
- If mass transfer determines the overall rate, the current is determined by the mass transfer rate

- 전극 전위는 전극 내부에 존재하는 전자 에너지의 표현이다
- 전기화학 반응은 전극 표면 근처에서만 가능하다
- 전기화학 반응은 여러 단계를 거쳐서 진행된다
- 전류는 반응 속도의 표현이다
- 전류는 전기화학 셀 내에서 닫힌 고리(closed loop)를 형성하며 흐른다
- 전하 전달이 전체 속도를 결정할 경우 전극 전위를 변화시켜 전류의 크기를 조절할 수 있다
- 전극 전위와 전류를 동시에 조절할 수 없다
- 물질 전달이 전체 속도를 결정할 경우 전류는 물질 전달 속도에 의해 결정된다

Electrochemical systems

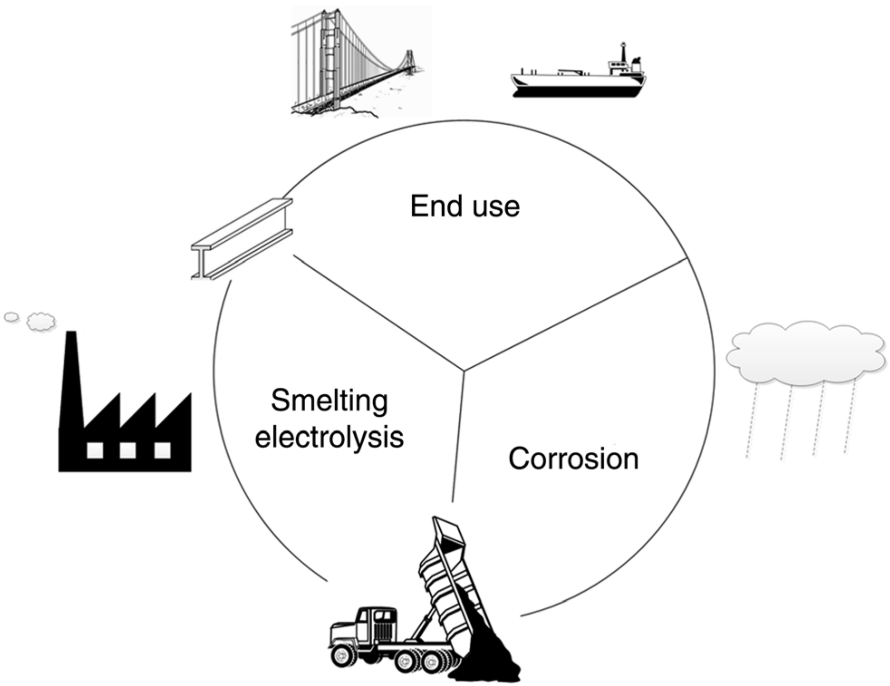


Figure 1.2 Life cycle of metals. Many of the processes are electrochemical.

Electrical quantities

(1) Electric charge & current

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

$$I = dq/dt$$

$$q = \int I dt \qquad C = A \cdot s$$

Current density (unit: A/cm^2): $i = I/A$, 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, **E** (unit: V/m)

$$\mathbf{E} = -d\phi/dx$$

Electric field strength,

$$\mathbf{E} = \mathbf{F}/q = (1/4\pi\varepsilon\varepsilon_0)(q'/r^2)$$

e.g.: $q = 1.6 \times 10^{-19}$ C, water dielectric constant $\varepsilon = 78.5$, vacuum permittivity $\varepsilon_0 = 8.85 \times 10^{-12}\ C^2N^{-1}m^{-2}$, double layer distance $r = 10^{-9}$ m
$\rightarrow E = 2 \times 10^7$ V/m $\rightarrow$ potential difference $\Delta\varphi = 20$ mV

(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), $1/\kappa$; 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

$$\text{Power (watts)} = I^2R$$

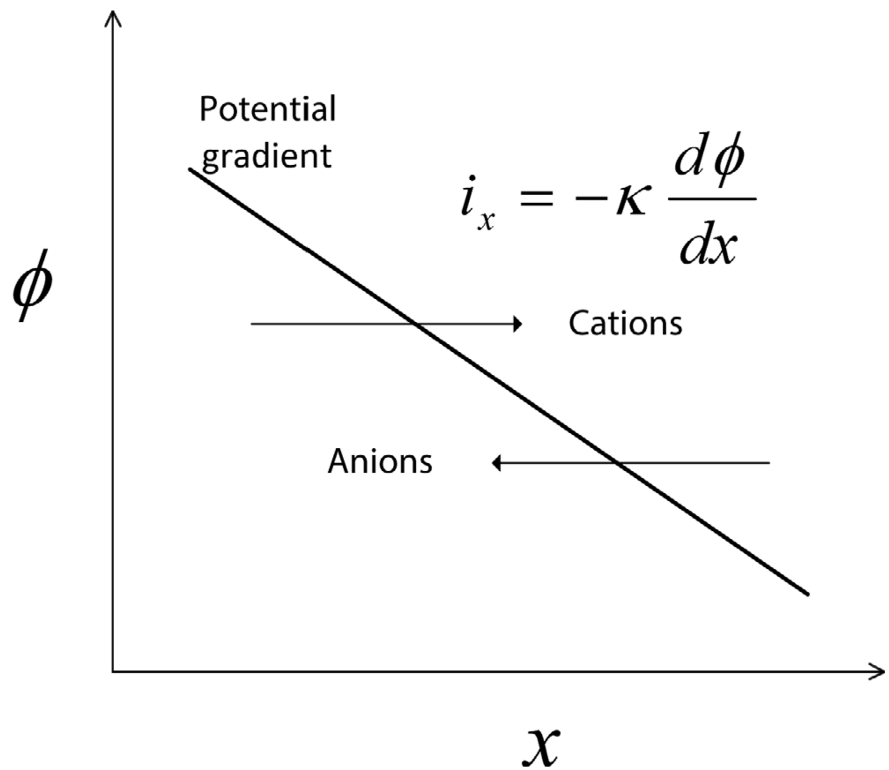


Figure 1.3 Gradient in potential and flow of current. Current flow is from left to right.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.

Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

(4) Power

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

Power = energy/time = work/time

Instantaneous power $P = dW/dt$

Average power $P = W/t$

Unit: watt (W) = J/s

1 horsepower (HP) = 746 W

Power ratings of various devices & animals

10^{18} W solar power input to earth

10^{12} W electricity capacity in USA (10^{11} W (125 GW), Korea)

10^{9} W large electric power plant

10^{7} W train

10^{5} W automobile

1000 W horse

100 W man/woman resting

0.1~1 W Si solar cell

0.01 W human heart

Energy storage(battery) and conversion(fuel cell)

Electric vehicle (battery) e.g. 300 km driving distance

40 kWh battery, Power 90 kW

(Energy density 140 Wh/kg, Power density 250 W/kg)

Battery weight 300 kg

Efficiency 7 km/kWh

FCV (fuel cell) e.g. 460 km driving distance

Power 113 kW

Power density 3 kW/*l*, 2kW/kg

FC weight 56 kg + (5 kg H_2 in tank (87 kg))

Efficiency 6 km/kWh

cf. Gasoline engine: ~800 km, 60~70 *liter* tank, 12 km/*liter*

Terminology and Unit

Terminology	Unit
Current (I)	Ampere (A)
Current density (i)	Ampere per m^2 (A/m^2)
Electric charge (q)	Coulomb (C = A·s)
Charge density (ρ)	Coulomb per m^3 (C/m^3)
Potential (ϕ)	Volt (V = J/C, or A·Ω)
Field strength (**E**)	Volt per meter (V/m)
Conductivity (κ)	Siemens per meter (S/m)
Resistance (R)	Ohm (Ω =1/S = V/A)
Conductance (G)	Siemens (S = A/V)
Permittivity (ε)	Farad per meter (F/m = C/V·m)
Energy (w)	Joule (J = V·C)
Power	Watt (W = J/s = A·V)
Capacitance (C)	Farad (F = C/V)

Faraday's law (페러데이 법칙)

charge(Q, C(1 C = 6.24 x 10^{18} 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)"

$$F = N_A Q_e = (6.02 \times 10^{23}\ mol^{-1})(1.6022 \times 10^{-19}\ C) = 96{,}485\ C \cdot mol^{-1}$$

F: Faraday's constant

Charge $Q = nFN$ Faraday's law

N: # of moles (N = m/M), n: # of electrons involved in reaction

전류(I) = dQ/dt = nF(dN/dt) [**단위**: A = C/s]

Reaction rate (mol/s) = dN/dt = i/nF

- Current (i) : the rate of the electrode reactions
- Charge (q or Q) → extent of chemical change at each electrode. The charge required to convert m mol of starting material to product in an ne^- electrode reaction is calculated using Faraday's law of electrolysis

$$q = \int i dt = mnF / M \qquad \text{for time t}$$

where F: Faraday constant (96485 C mol^{-1})

e.g. if the current is 1 A for $2H^+ + 2e^- \rightarrow H_2$

1) Current: 1 A = 1 C/s
2) Mole of electron: $1 \text{ C/s} \times \frac{1}{96485\ C/mol} = 1.036 \times 10^{-5}\ mol/s$
3) Mole of H_2: $1.036 \times 10^{-5} mol/s \times \frac{1}{2} = 5.182 \times 10^{-6} mol/s$

$$i(\text{amperes}) = \frac{dQ}{dt}(\text{coulombs/s})$$

$$\frac{Q}{nF}\frac{(\text{coulombs})}{(\text{coulombs/mol})} = N(\text{mol electrolyzed})$$

$$\text{Rate (mol/s)} = \frac{dN}{dt} = \frac{i}{nF}$$

Mass of I species

$$m_i = M_i Q / nF$$

m_i: mass, M_i: molecular weight

Illustration 1.2, 1.3, 1.4

It is strongly recommended to solve the textbook example(Illustration)!!

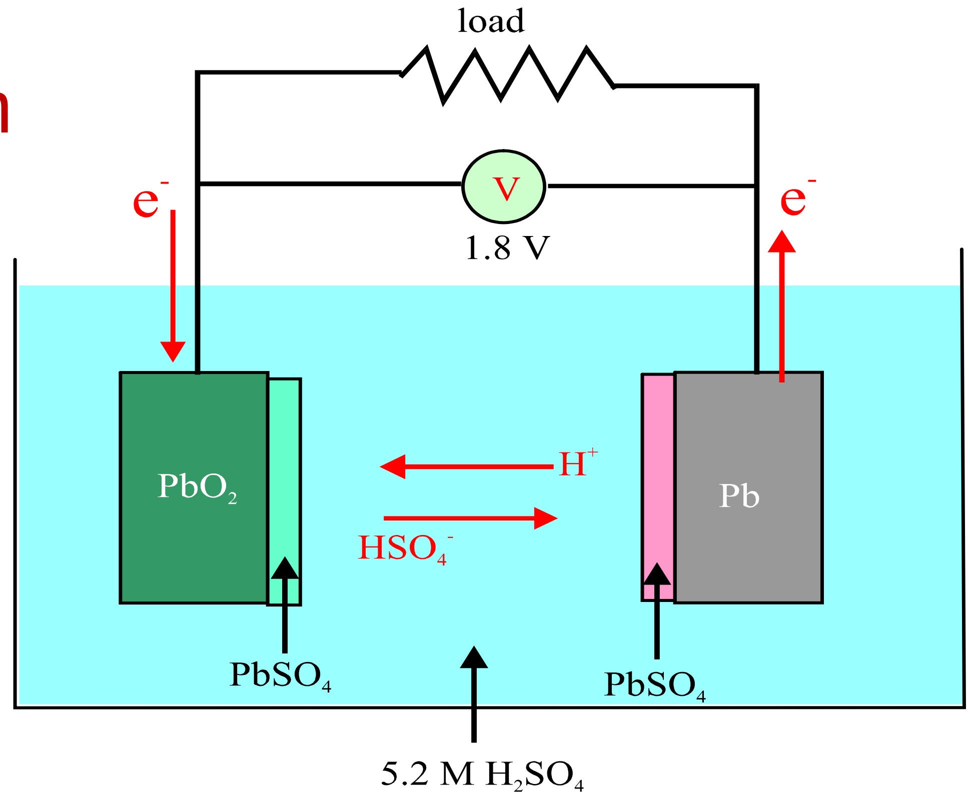
Faradaic efficiency

$$\eta_f = \frac{\text{amount of desired material produced}}{\text{amount that could be produced with the coulombs supplied}}$$

Illustration 1.5, 1.6

Electrochemical system

e.g., lead/acid cell (car battery)



Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow 2e^- + PbSO_4(s)$

Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

Cell: $PbO_2(s) + Pb(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

Right-hand electrode: electrons produced: **oxidation**, “**anode**” **negative**

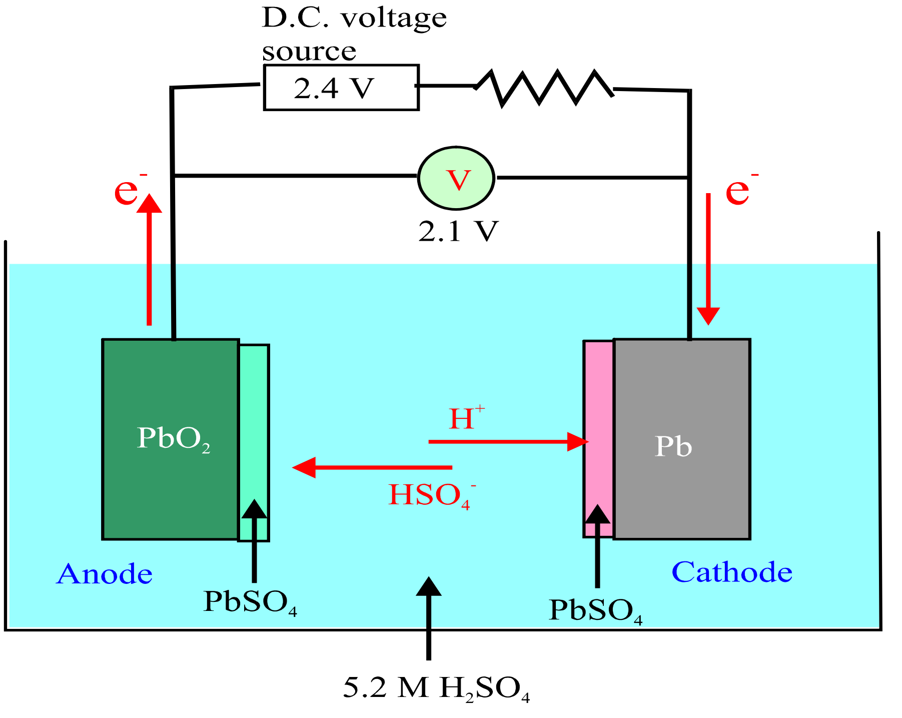
Left-hand electrode: electrons consumed; **reduction**, “**cathode**” **positive**

2.0 V without current flow, 1.8 V with current flow (load); “**polarization**”

Galvanic cell: a cell which provides energy in this way, “**discharge**” **방전**

"**charge**": current flow in the opposite direction by using an external source; **Electrolytic cell**; opposite direction to its spontaneous motion

PbO_2 : anode, Pb: cathode



2.0 V; perfect balance between the applied and cell voltages, no current flow → equilibrium cell voltage or reversible cell voltage or null voltage or rest voltage or "open-circuit voltage (OCV)"(since no current flows, it makes no difference if the circuit is interrupted, as by opening the switch)

Types of electrochemical cells

(i) Galvanic cell: reactions occur spontaneously at the electrodes when they are connected externally by a conductor. Converting chemical energy into electrical energy. e.g., primary battery, secondary battery (discharging), fuel cell

(ii) Electrolytic cell: reactions are effected by an external voltage. Electrical energy to chemical reactions. e.g., electrolytic syntheses, electrorefining (e.g., copper), electroplating, secondary battery (charging)

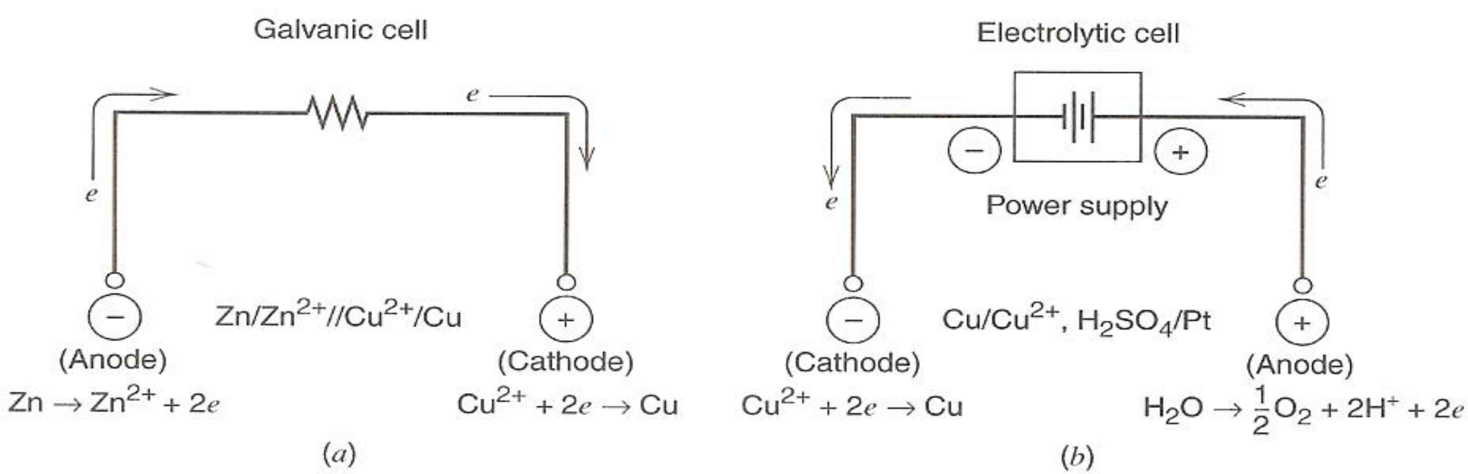
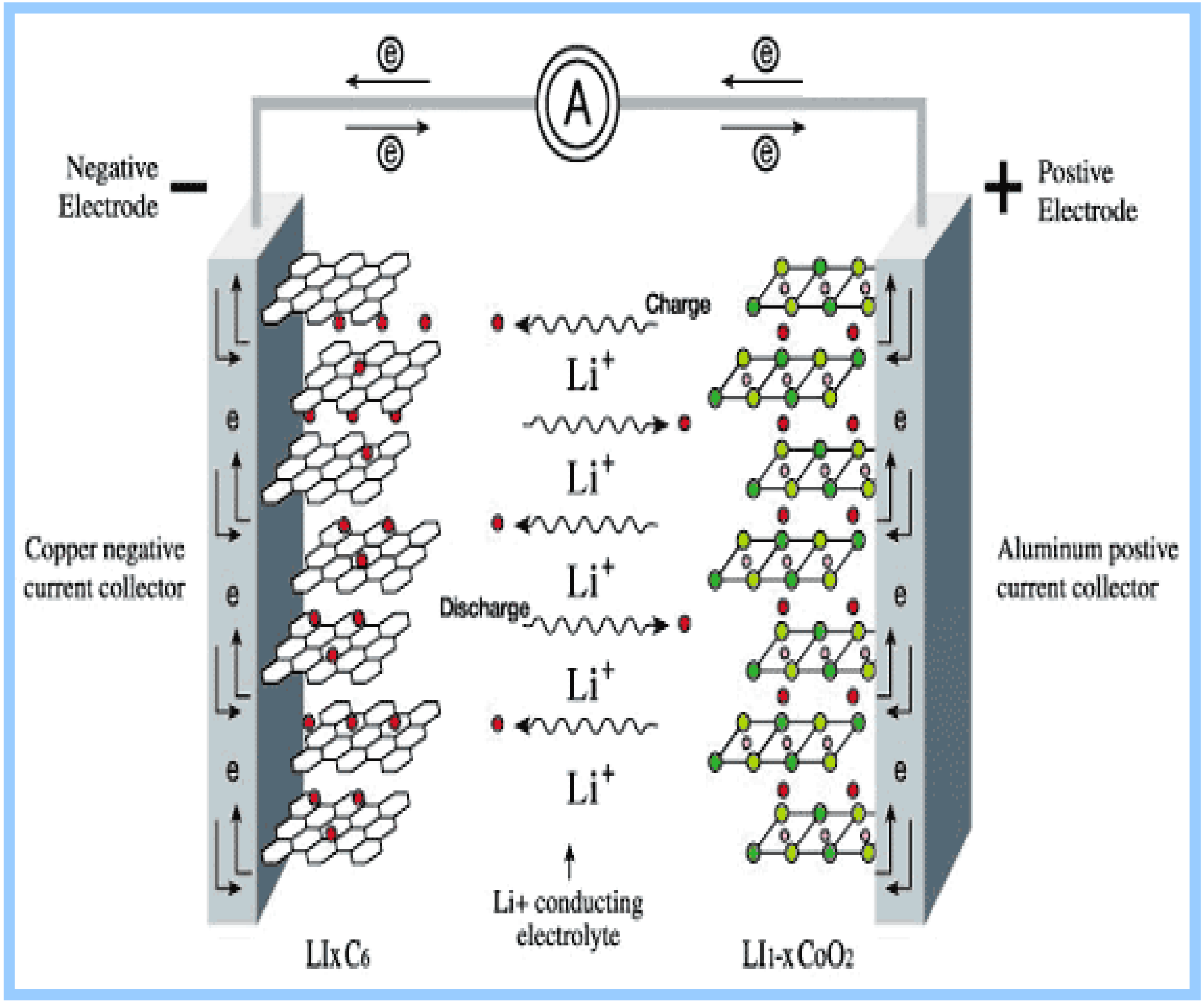


Figure 1.3.1 (*a*) Galvanic and (*b*) electrolytic cells.

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

Lithium rechargeable battery



$$LiCoO_2 + C_6 \underset{\text{discharge}}{\overset{\text{charge}}{\leftrightarrow}} Li_{1-x}CoO_2 + Li_xC_6$$

2019 Nobel Proze in Chemistry

Li secondary battery

존 굿이너프

John B. Goodenough

스탠리 휘팅햄

M. Stanley Whittingham

아키라 요시노

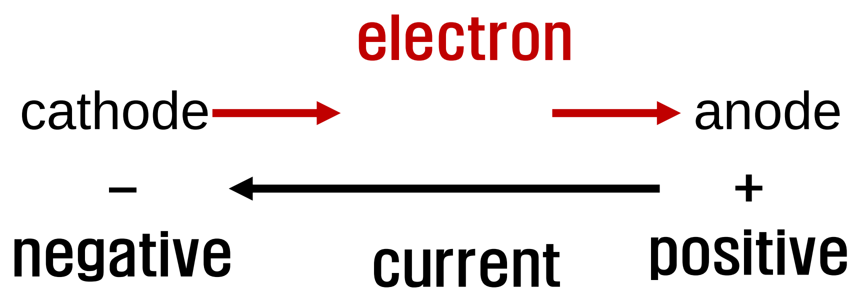
Akira Yoshino

Positive electrode(+) and negative electrode(-)

양극, 음극, 산화극(anode), 환원극(cathode)

1834 William Whewell (+Faraday)

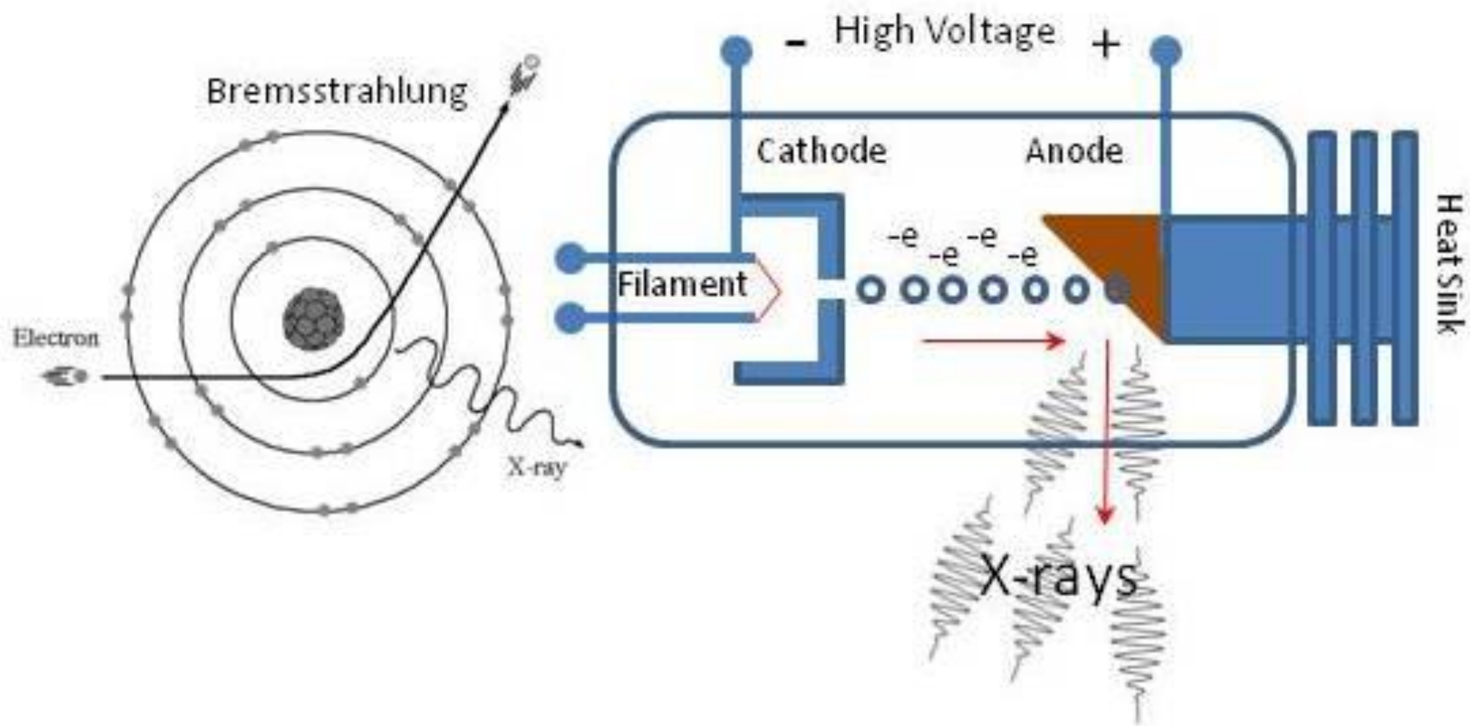
-cathode(Greek kathodos(descent, way down): current exits/emits (to electric device or chemical reaction)



✓Humphrey Davy, 1778-1829): Proposed oxygen generating electrode as positive and hydrogen generating electrode as negative during electrolysis of water → positively charged hydrogen ions move to the negative

✓**참고**: **데이비**(Humphrey Davy, 1778-1829): **물의 전기분해시 산소발생 전극을 양극**(positive), **수소발생 전극을 음극**(negative)**으로 제안** → **양의 전하를 띤 수소이온이 음극으로 이동**

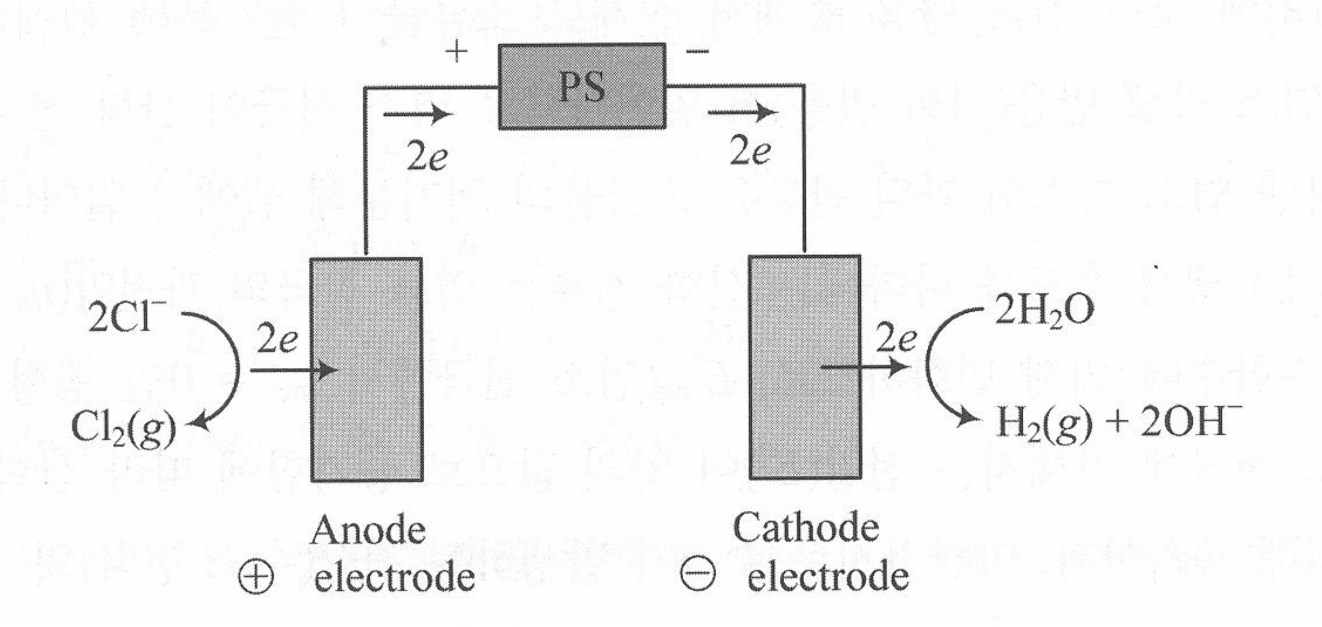
positive, negative, anode, cathode



http://www.hardhack.org.au/xraydtt

Electrolytic cell: positive, negative, anode, cathode

✓Sea water(NaCl) electrolysis



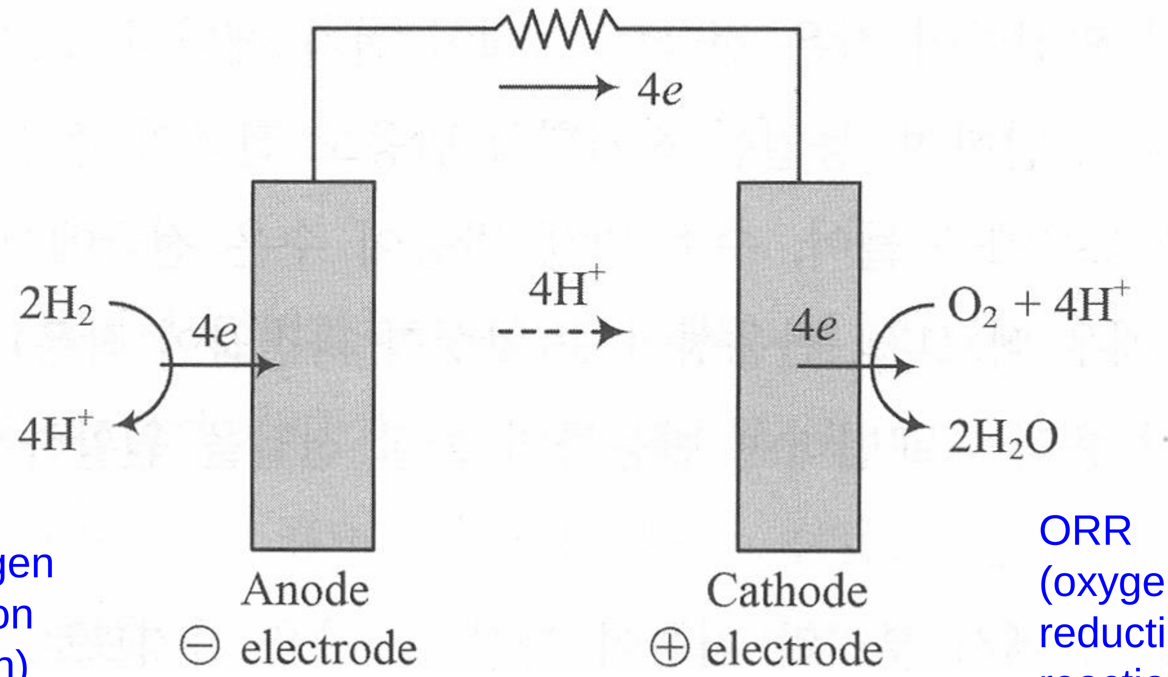
✓Water electrolysis:

- **산소발생 전극**(OER(oxygen evolution reaction), anode, oxidation) **양극**(positive)
- **수소발생 전극**(HER(hydrogen), cathode, reduction) **음극**(negative)

Oh, ch.1

Galvanic cell: positive, negative, anode, cathode

✓Fuel cell



HOR (hydrogen oxidation reaction)

ORR (oxygen reduction reaction)

Oh, ch.1

Rechargeable battery: galvanic cell + electrolytic cell

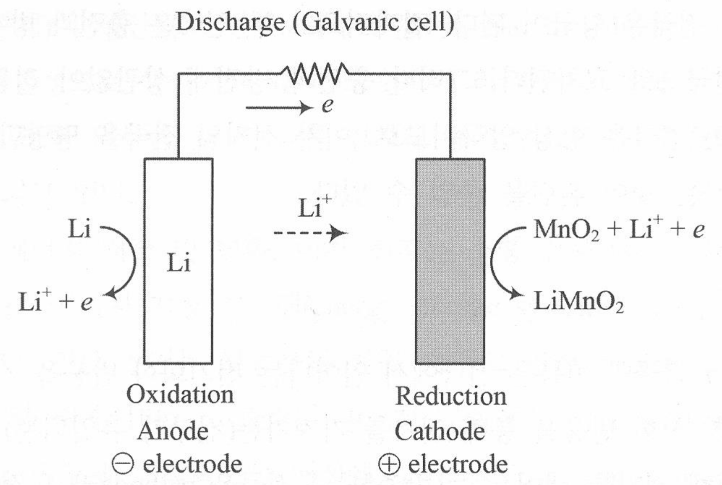


그림 1-21 Li/MnO_2 이차 전지의 방전 과정에서 전극 반응과 전극의 명칭

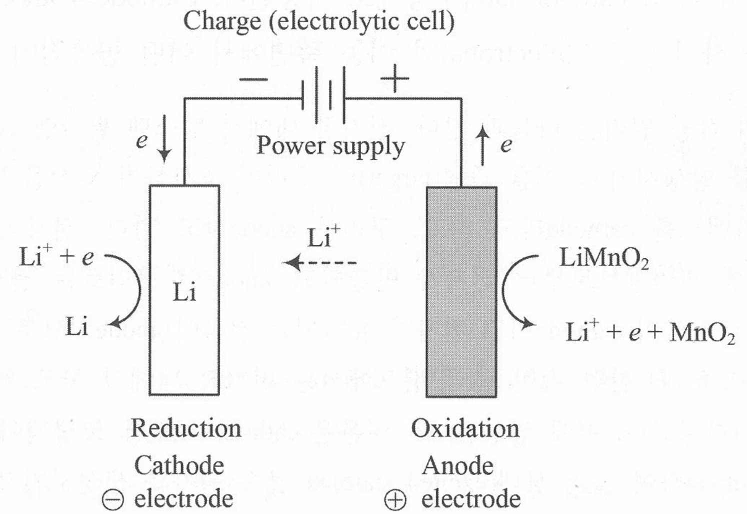


그림 1-22 Li/MnO_2 이차 전지의 충전 과정에서 전극 반응과 전극의 명칭

Oh, ch.1

Positive, negative, **산화극**(anode), **환원극**(cathode)

Anode	Cathode
The anode is the electrode where electricity moves into.	The cathode is the electrode where electricity is given out or flows out of.
A anode is usually the positive side in electrolytic cell.	A cathode is a negative side in electrolytic cell.
It acts as an electron donor.	It acts as an electron acceptor.
An oxidation reaction takes place at the anode.	A reduction reaction takes place at the cathode.
In galvanic cells, an anode can become a negative.	In galvanic cells, a cathode can become an positive.

https://byjus.com/chemistry/cathode-and-anode/

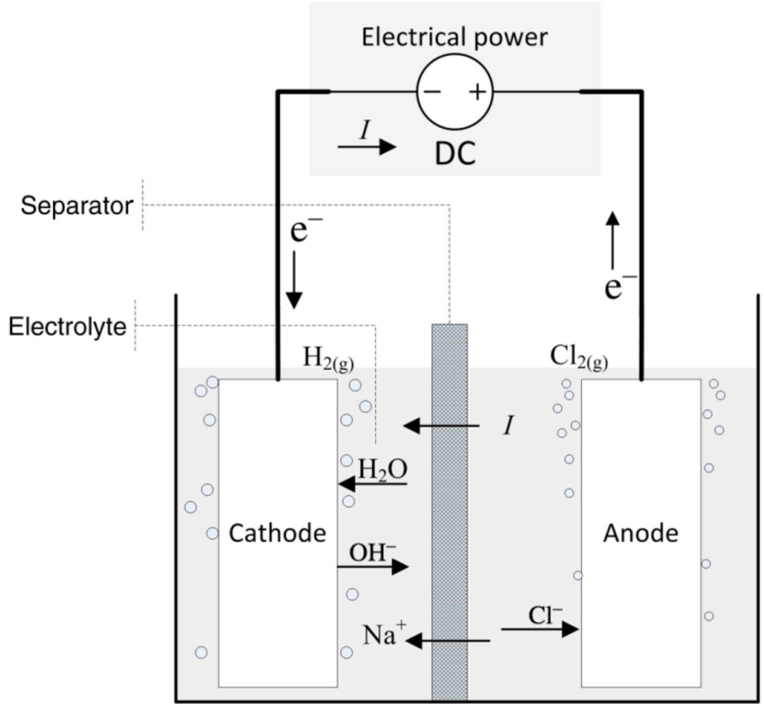


Figure 1.4 Electrochemical cell for the chlor-alkali process.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.

Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

Chloro-alkali process

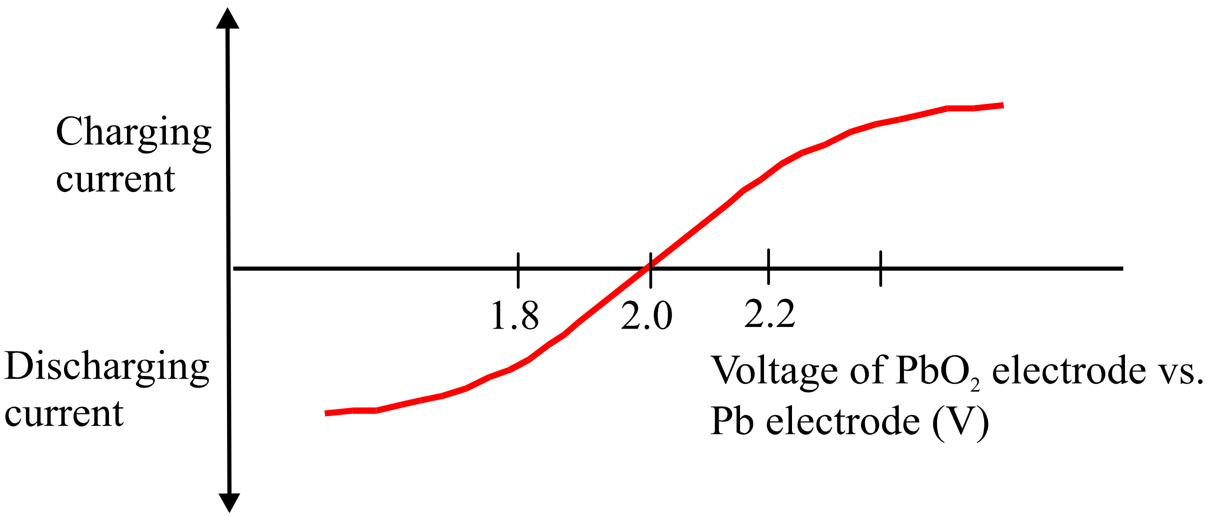
Anode: $2Cl^- \rightarrow 2e^- + Cl_2$

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Overall: $2H_2O + 2Cl^- \rightarrow Cl_2 + H_2 + 2OH^-$

Voltammetry: I-V relation

Plot of cell currents versus the cell voltages (volt + am(pere) + mogram)



Not linear → electrochemical cells do not obey Ohm's law

Overpotential (or overvoltage, polarization) $\eta = E - E_{eq}$

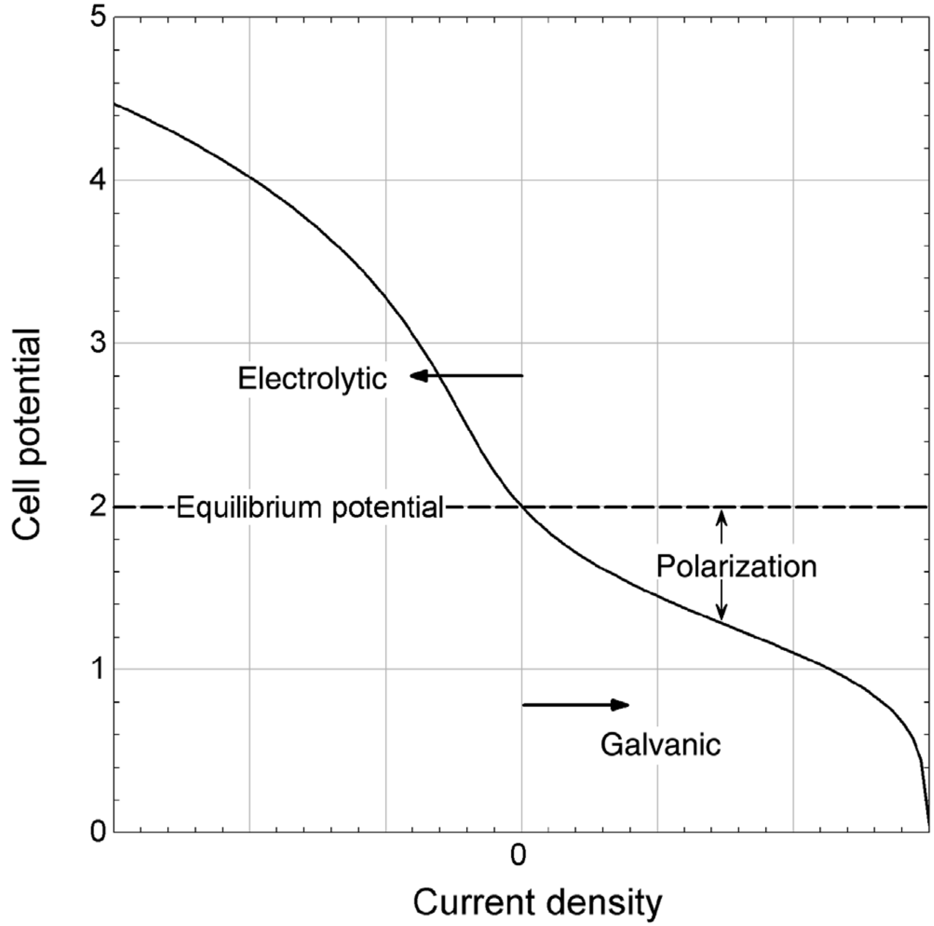


Figure 1.5 Representative relationship between current and potential at steady state. The dividing line between galvanic and electrolytic operation is at a current density of zero.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.

Companion Website: www.wiley.com/go/fuller/electrochemicalengineering