



박막및나노표면공학-강의자료
제2장 전기도금

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전기화학반응 프로세스의 특징

건식프로세스와 비교한 습식프로세스(수용액 반응)의 특징은 다음과 같다.

- ① 금속은 이온의 형태로 존재한다. Cu^{2+}
- ② 반응에서는 항상 물의 존재를 고려해 놓지 않으면 안 된다. $\text{H}_2(\text{g}), \text{O}_2(\text{g}), \text{pH}$ 변화
반응식 중에 H_2O 가 들어가는 것도 있고, H^+ 또는 OH^- 가 관여한다.
- ③ 반응은 상온에서 진행한다(100°C 이하). 고온이면 수용액의 안전성 문제
- ④ 반응은 전자의 교환에 의해서 진행하기 때문에 이것을 제어하는 것에 따라 반응을 세밀하게 관리할 수 있다. 산화 환원반응
- ⑤ 반응속도는 직접전류에 의해 측정 가능하고, 반응의 구동력도 전위를 제어하는 것에 따라 자유로이 변화시킬 수 있다. 전류 조절로 반응속도 조절 가능

Definition

① Electrodeposition (전기증착);

The deposition of a substance (mainly metals or oxides) on an electrode by the action of electricity (especially by electrolysis)

② Electrolysis (전기분해);

Lysis of a bond produced by the passage of an electric current

③ Electrolyte (전해질);

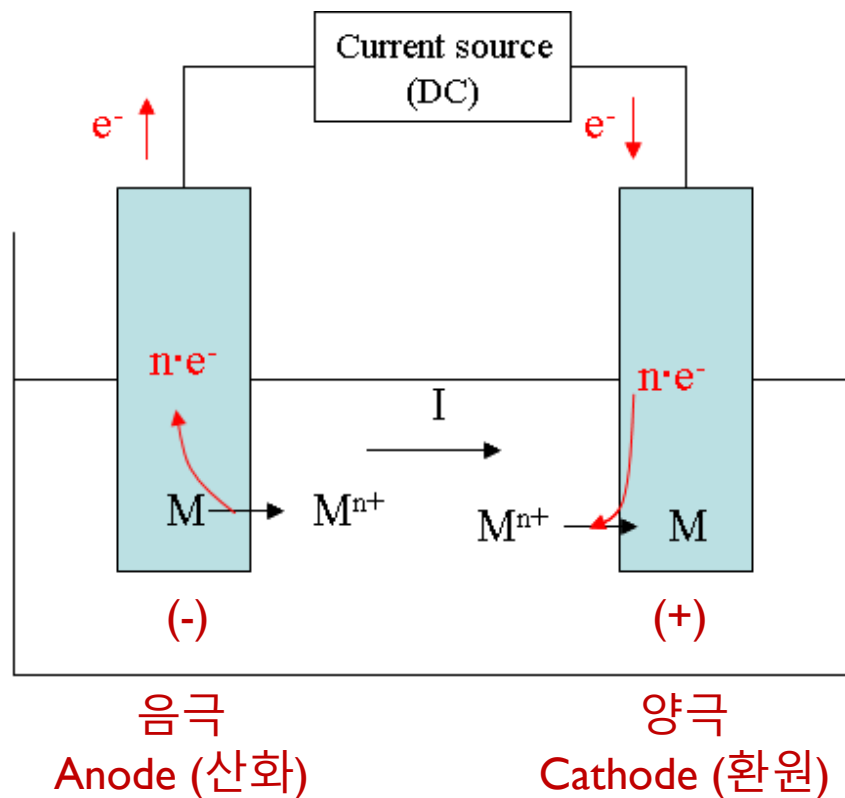
A solution that conducts electricity

④ Electrode (전극);

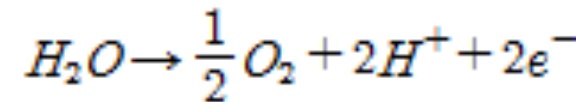
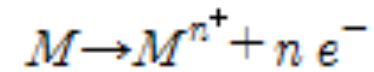
A conductor used to make electrical contact with some part of a circuit

Electrodeposition, Electroplating

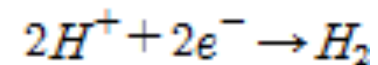
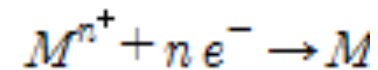
Electrodeposition cell



- anode reaction; oxidation



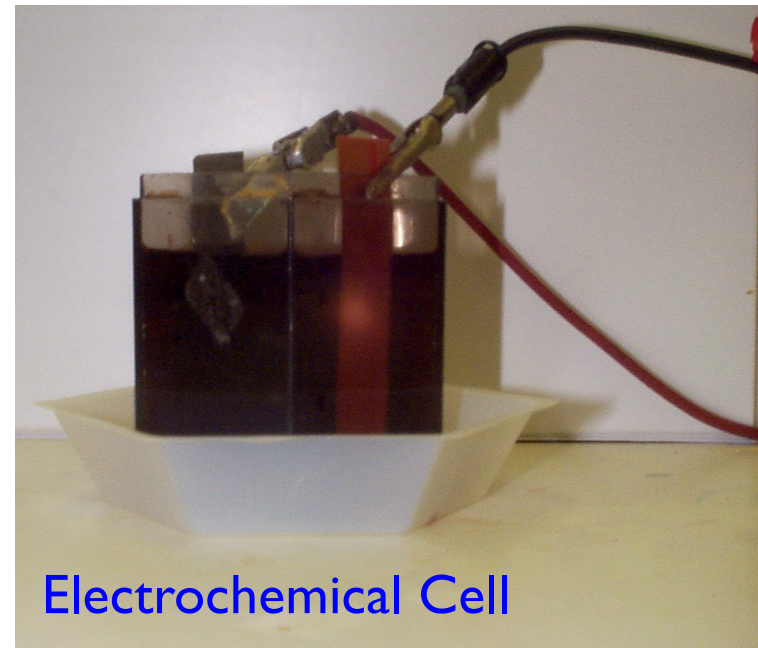
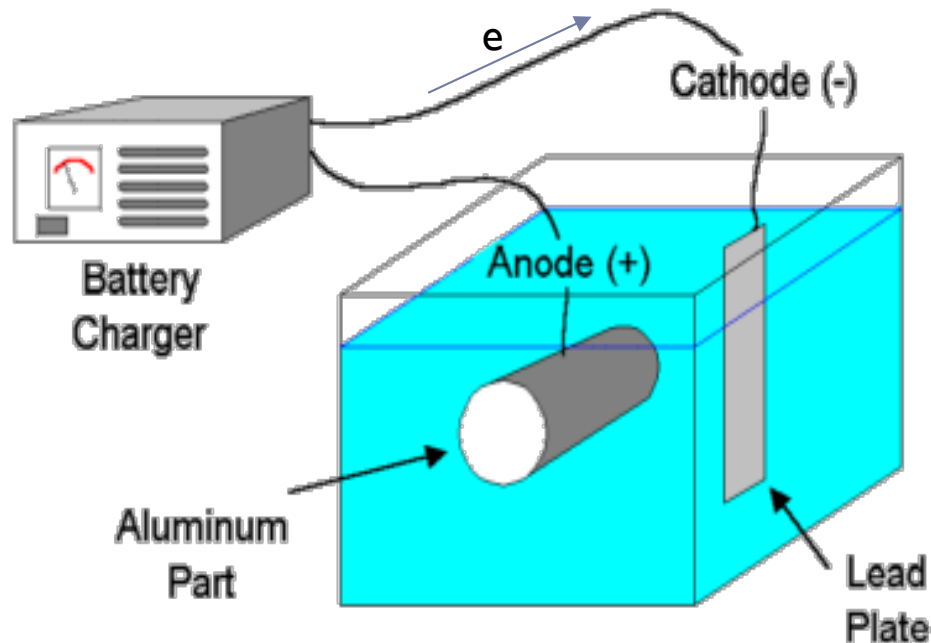
- cathode reaction; reduction



Equipments for Electrodeposition

Electrodeposition cell 의 구성

- Power supply (DC)
- Cathode (환원) → 도금을 당할 물체
- Anode (산화) → 금속이온 공급(도금용)
- Plating bath (금속이온)



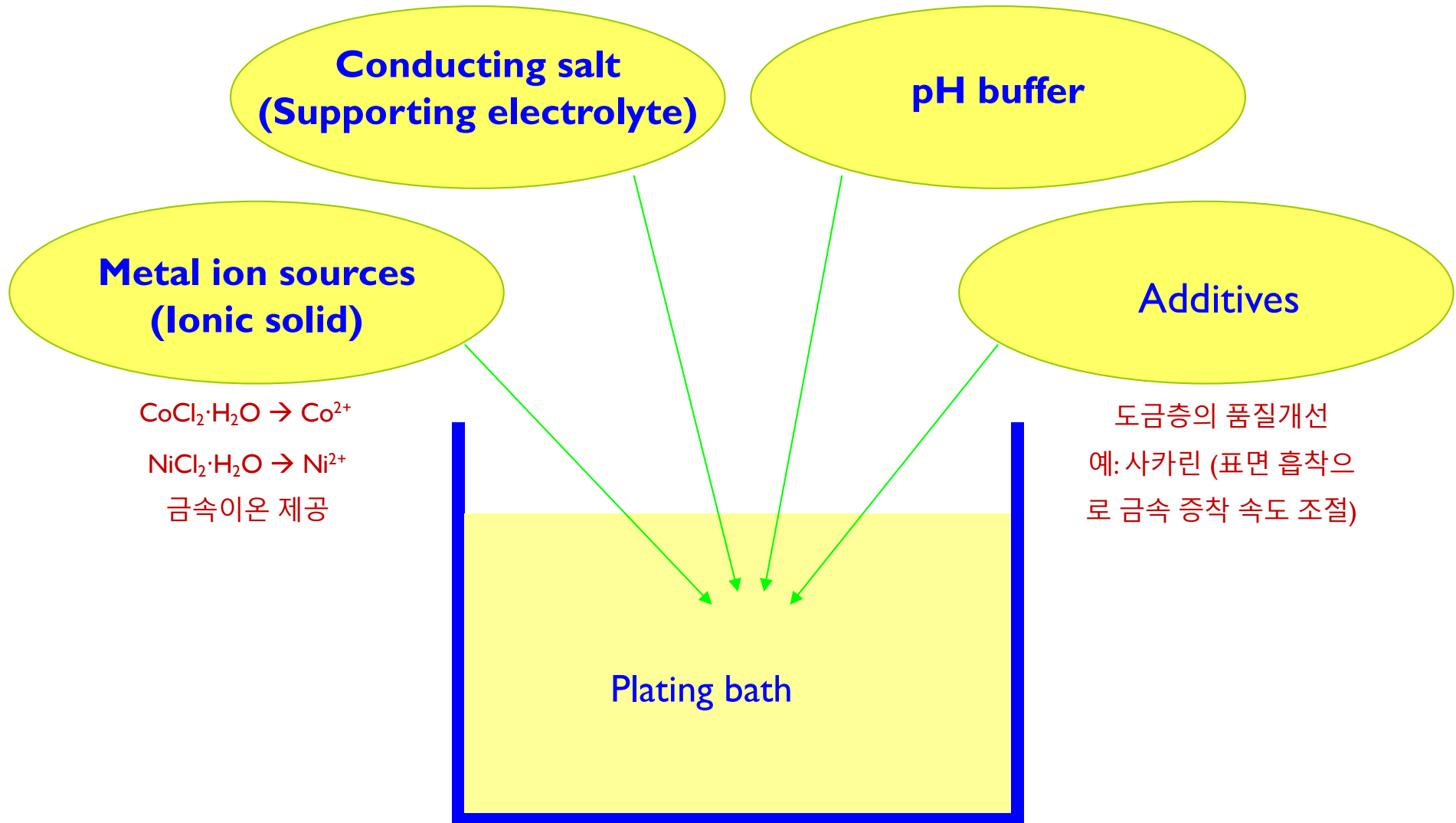
Electrodeposition Solution

용액 pH 안정화 : H_3BO_3 (붕산)

강산 \rightarrow 수소발생 경쟁

강염기 \rightarrow $\text{M}_x(\text{OH})_y$ 생성

전도성 증가 (이온화가 쉬운): NaCl , Na_2SO_4



Electroplating Bath

① Metal Ion Source

ex) CoNi thin film alloy를 도금하고자 할 때

▶ bath type 결정

chloride bath, sulfur bath, sulfamate bath, Watts-type bath 등 중에서 어느 것?

높은전도성 환경친화 균일한 도금층 생성 균일한 도금층 생성
빠른 도금속도 저렴한비용

▶ chloride bath로 결정했다고 가정, metal ion sources 인 chemicals 를 선택

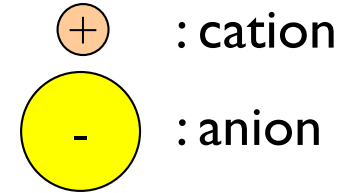
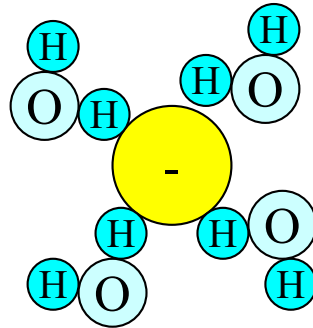
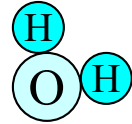
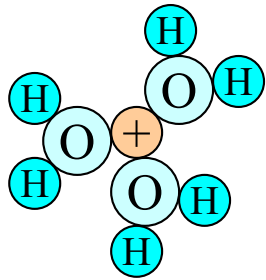
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Co source}$

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Ni source}$

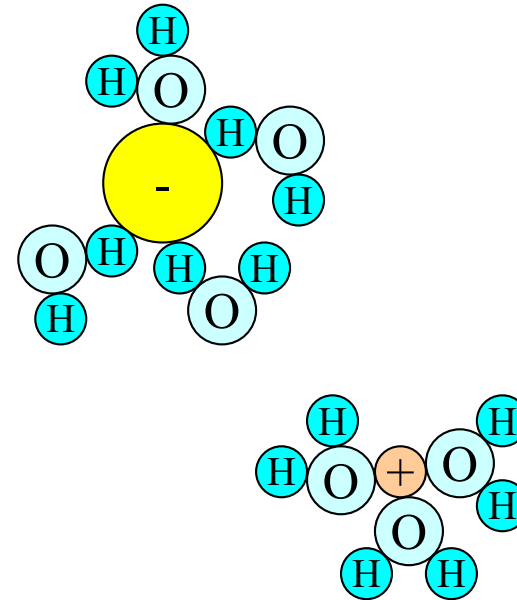
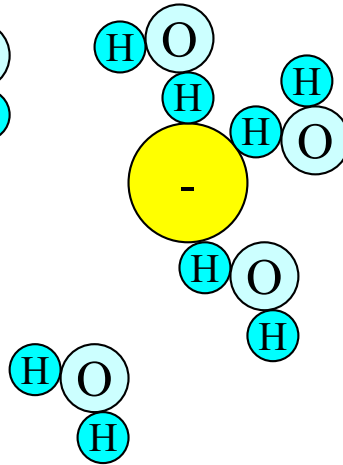
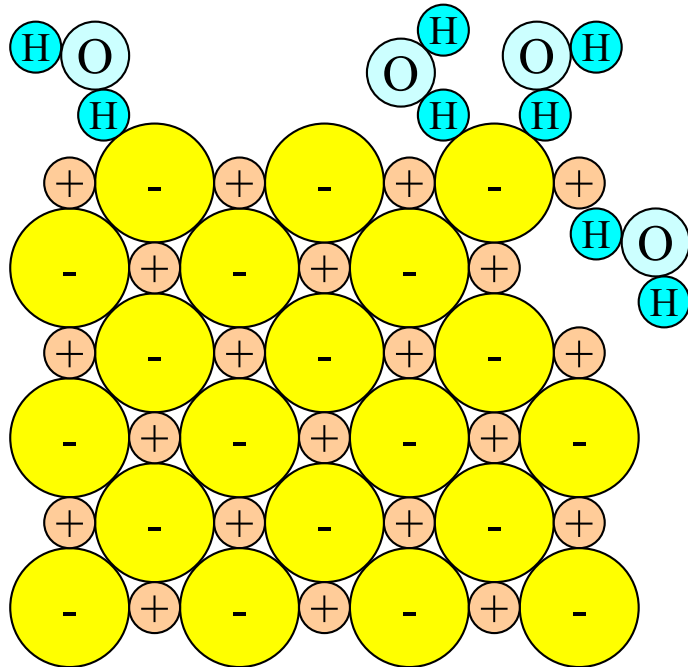
▶ CoCl_2 and $\text{NiCl}_2 \rightarrow$ ionic solid; ionic bonding

Ionic bonding; a primary bond arising from the **electrostatic attraction** between two oppositely charged ions.

Ionic Solid in Water



**Example: CoCl_2 , NaCl
 CoSO_4 , NaSO_4**



Electroplating Bath

② Conducting salts (supporting electrolyte)

; 전류가 흐르도록 하기 위하여 넣어주는 화학약품

ex) chloride bath; NaCl

sulfate bath; Na₂SO₄

③ pH buffer

; a defined solution that resists change in pH when a small amount of an acid or base is added or when solution is diluted.

This is very useful for maintaining the pH for a reaction at an optimum value.

ex) H₃BO₃

④ Additives

; 전기도금에 의해 음극에 deposit 된 film 의 stress 나 surface 를 미려하게 하기 위하여 첨가하는 첨가제

ex) Saccharin

Electroplating Bath- examples

- Chloride bath

0.2 M CoCl_2
0.206 M NiCl_2
0.7M NaCl
0.4 M H_3BO_3
0.0048 M Saccharin

- Sulfate bath,

0.2 M CoSO_4
0.206 M NiSO_4
0.7M NaSO_4
0.4 M H_3BO_3
0.0048 M Saccharin

- Sulfamate bath,

0.2 M $\text{Co}(\text{NH}_2\text{SO}_3)_2$
0.206 M $\text{Ni}(\text{NH}_2\text{SO}_3)_2$
0.7M $\text{Na}\cdot\text{NH}_2\text{SO}_3$
0.4 M H_3BO_3
0.0048 M Saccharin

Electroplating Bath- examples

- ▶ Ni (pure) electrodeposition

- ⌘ Calculation of each chemicals to make Ni plating bath

- 0.2M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$

- 0.7M NaCl

- 0.4M H_3BO_3

- 1g/L Saccharin (Sodium O-Benzoic Sulfinide) ; 205.16 g/mol

- ▶ case 1) Make total 1 liter solution

- ▶ case 2) Make total 300 mL solution

Molarity, M (몰농도)

※ Molarity, M (mole/l)

; a ration giving the **number of moles of solute (용질)** per **1 liter of solution (용액)**

$$\text{Molarity}(M) = \frac{\text{mole of solute}}{\ell \text{ of solution}} \text{ (mole / } \ell \text{)}$$

ex) a solution containing 1 mole of KBr in 1L of solution → 1M(molar) solution

※ Concept of mole (mole)

6.02×10^{23} iron atoms \Rightarrow 1 mole iron atoms

- Avogadro's number; 6.02×10^{23}

- A mole is 6.02×10^{23} objects.

ex) 1 mole atoms = 6.02×10^{23} atoms

- conversion factors $\frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ objects}}$ 또는 $\frac{6.02 \times 10^{23} \text{ objects}}{1 \text{ mole}}$



Mass of Mole (물질량, g/mol)

The molar mass of an element (when the element is in atomic form) is a mass in grams that is numerically equal to the atomic mass of the element.

Atomic weight

- Mass of 1 carbon atom = 12.011 amu (atomic mass unit)
 - Mass of 1 mole of carbon atom = 12.011 g/mol (molar mass)
- ex) 6.02×10^{23} Cl atoms = 1 mole Cl atoms = 35.453 g/mol
- ex) 44.0 g/mol = 1 mole CO₂

Atomic mass

$$\begin{aligned} \text{C}^{12} &= 12.0000 \text{ amu} \\ \text{C}^{13} &= 13.0034 \text{ amu} \end{aligned}$$

Atomic weight

$$\text{C} = 12.0110 \text{ amu (or g/mol)}$$

Mass of Mole

※ Formula mass (or formular weight, 화학식 질량);

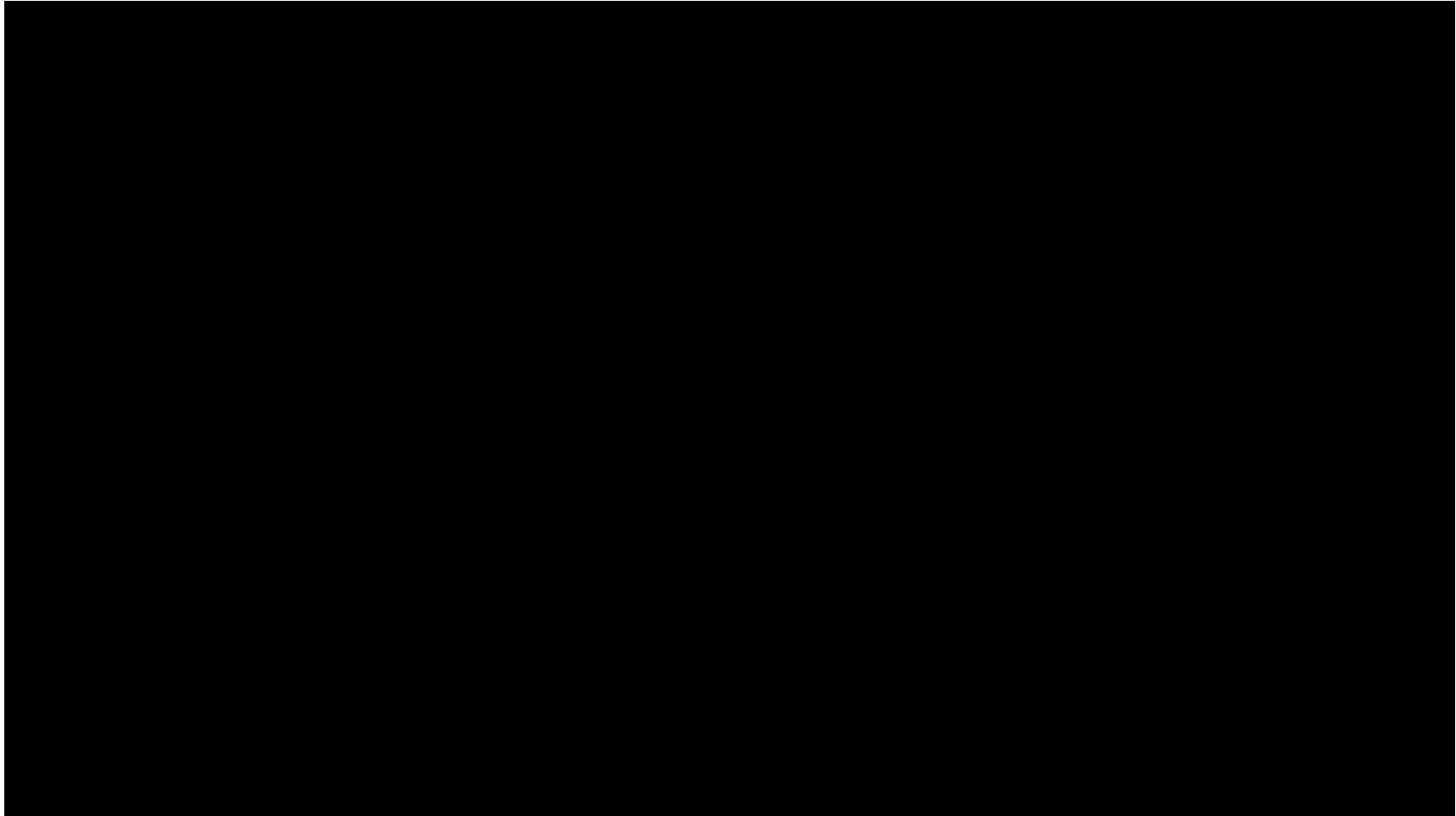
The sum of the atomic mass of the atoms present in one formula unit of the substance.

ex) $\text{Na}_2\text{S}_2\text{O}_3$

atomic weight of Na; 22.989768 g/mol, S; 32.066 g/mol, O;
15.9994 g/mol

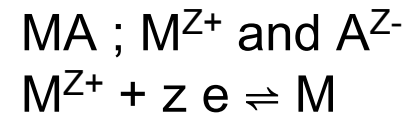
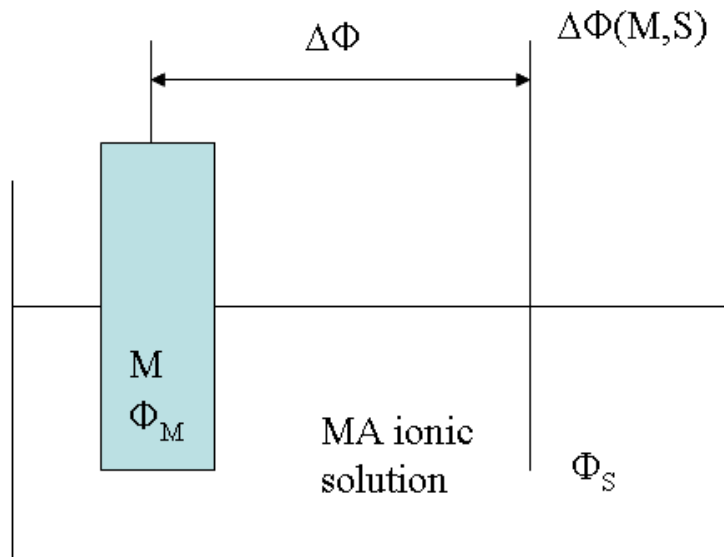
formula mass of $\text{Na}_2\text{S}_2\text{O}_3 =$

$$(22.989768 \times 2) + (32.066 \times 2) + (15.9994 \times 3) = 158.110 \text{ g/mol}$$



Easy Nickel And Copper Electroplating Method
<https://www.youtube.com/watch?v=Q8Xo43sfLgY>

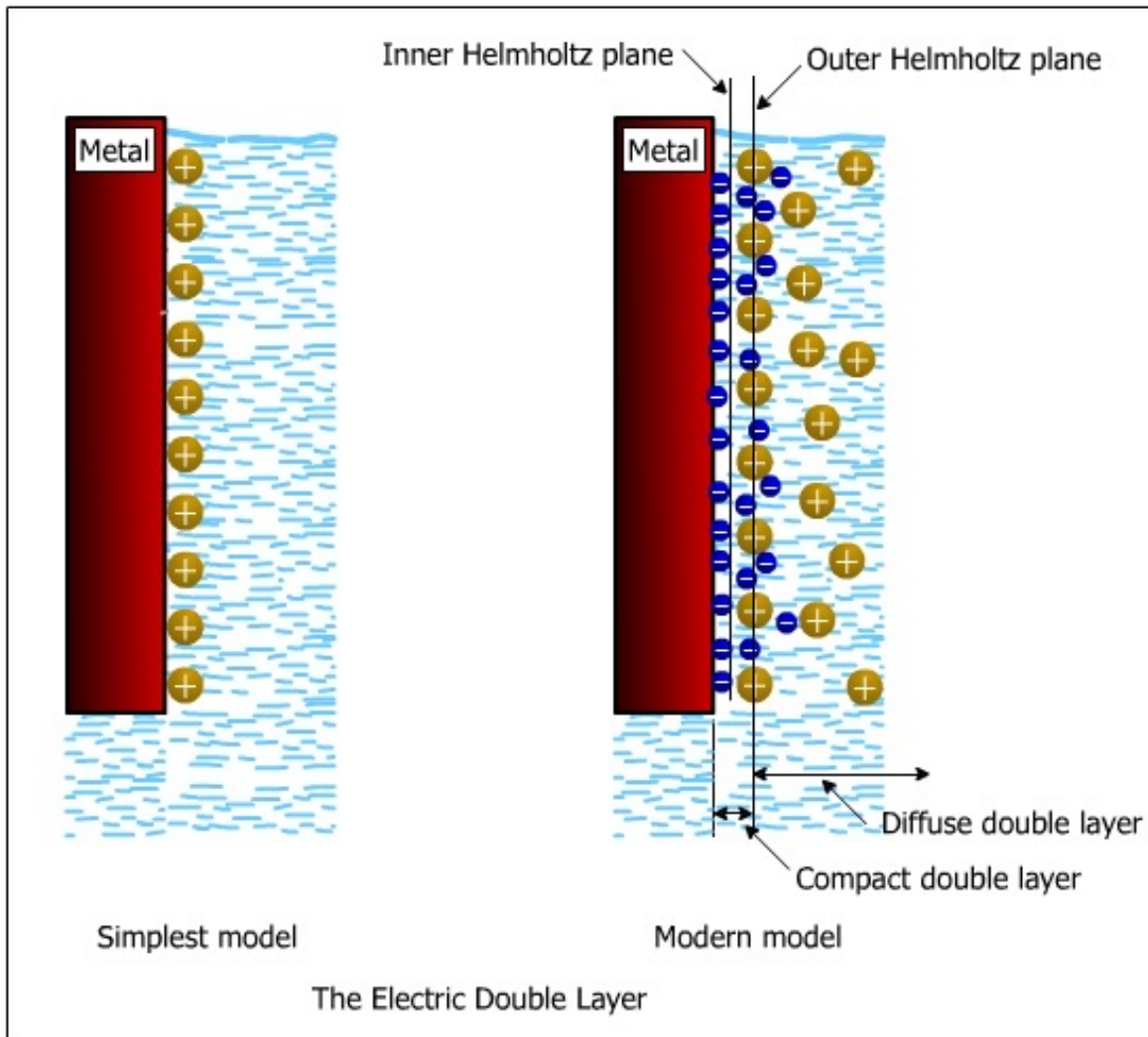
Electrode Potential (전극전위)



where M; a metal
z; number of e^- involved in the reaction

- ▶ Reduction; Reaction from left to the right **consumes electrons**.
- ▶ Oxidation; Reaction from right to the **left liberates electrons**.

Helmholtz Double Layer



- ▶ When a metal dissolves continuously, it may become increasingly **negatively charged because of passage of continuous positive ions in the solution**. The excess negative charge on the metal surface balances **the excess positive charge** and the solution side of the interface and hence, a separation of charges exists.
- ▶ The electrons orient themselves opposite a layer of cations of equal and opposite charges on the solution side of the interface. The electric field which is created consists of **two layers of charges**; hence it has been given a name double layer. The separation of charges in the double layer **can be compared to parallel plates in a capacitor** as it was done by Helmholtz. The double layer is also called Helmholtz Double Layer.

<http://faculty.kfupm.edu.sa/ME/hussaini/Corrosion%20Engineering/02.05.04.htm>

Electrode Potential

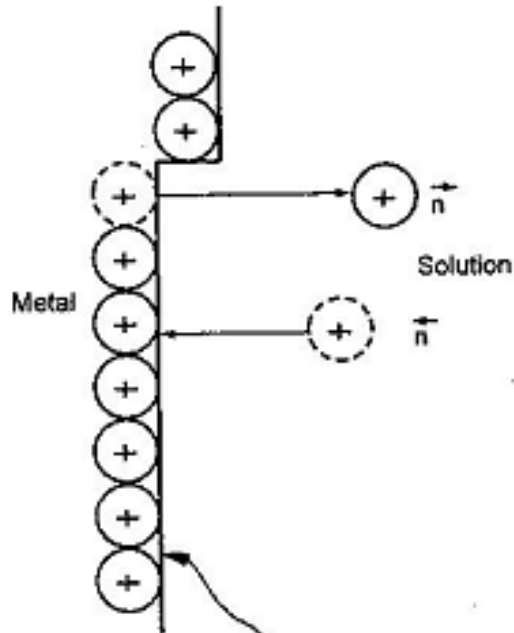


Figure 1 Formation of metal-solution interphase; equilibrium state: $\bar{n} = \bar{n}$.

\bar{n} ; number of M^{Z+} ions which leave crystal lattice
 \bar{n} ; number of M^{Z+} ions which enter crystal lattice

at the dynamic equilibrium,

$$\bar{n} = \bar{n}$$

The inter-phase region is neutral at equilibrium.

$$q_M = -q_S$$

q_M^- ; the charge on the metal per unit area

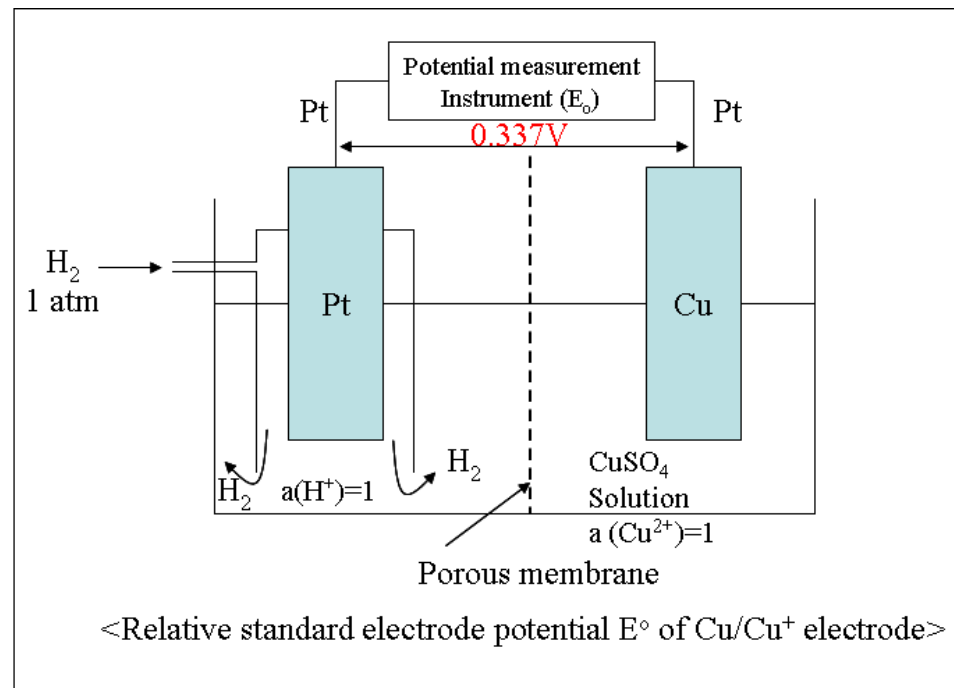
q_S^+ ; the charge per unit area on the solution side of the inter-phase

$$\Delta\Phi(M,S) = \Phi_M - \Phi_S$$

; the potential difference between the potentials of metal, Φ_M , and the solution, Φ_S , from the result of the charging of the inter-phase

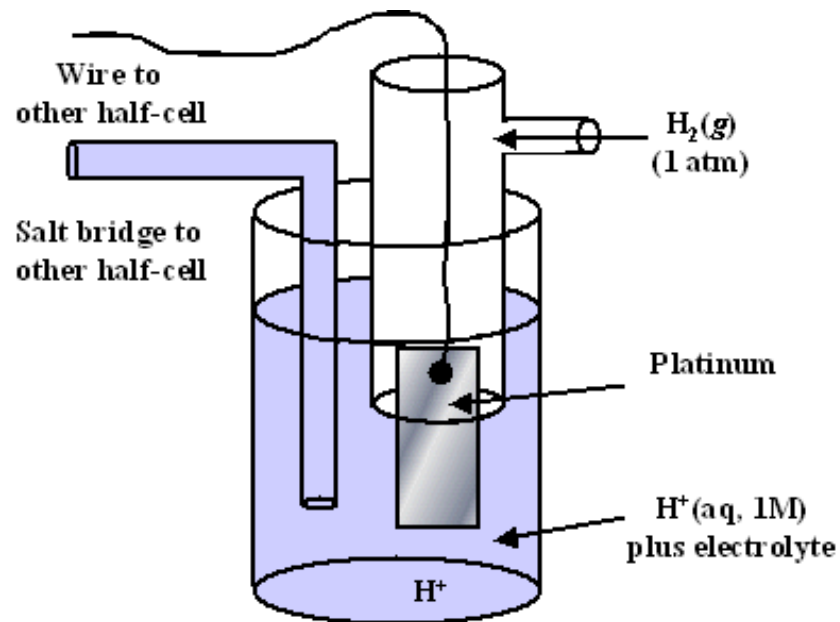
Electrode Potential

In order to measure the potential difference of an inter-phase, **one must connect it to another one** and thus form an electrochemical cell.



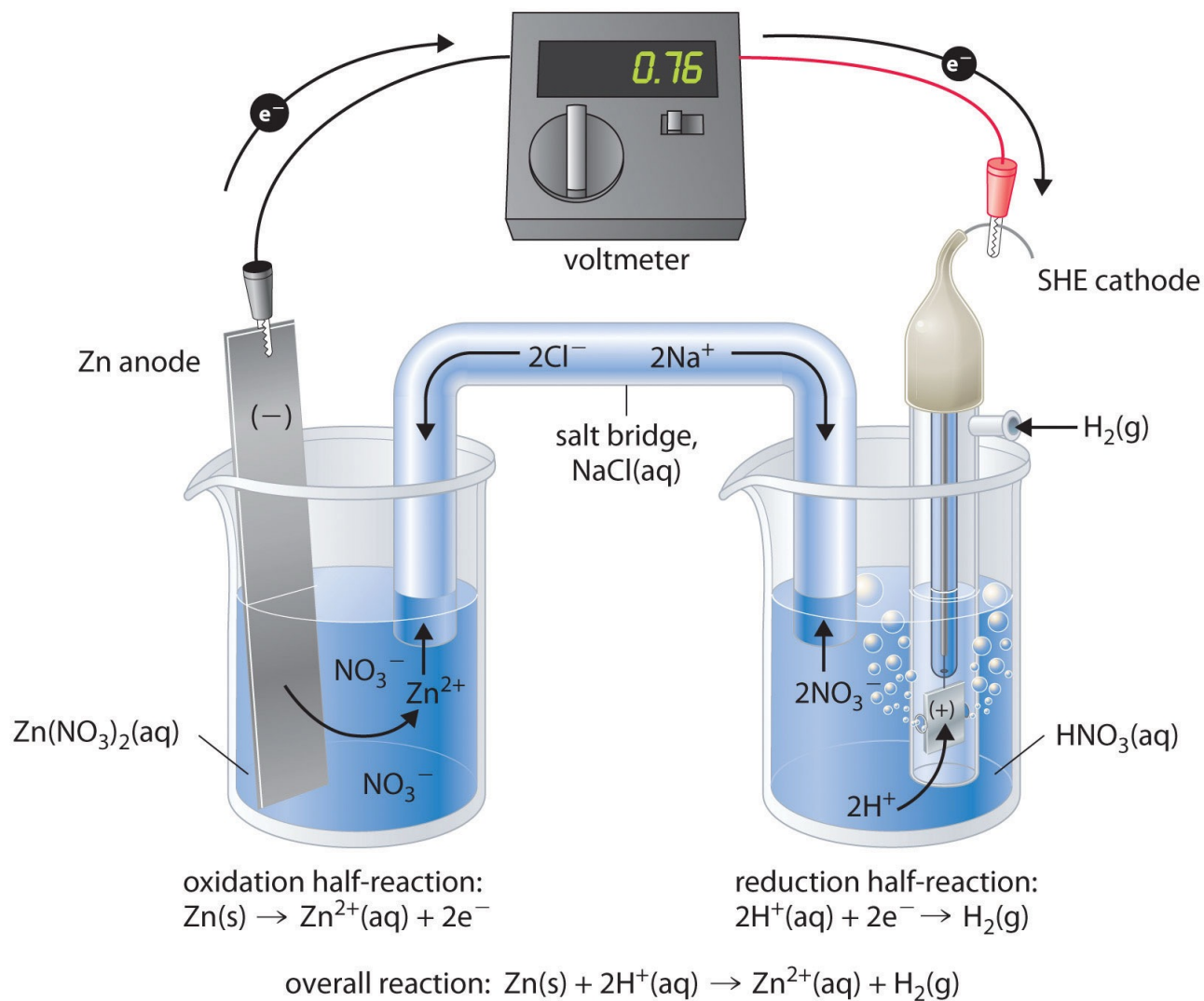
standard hydrogen electrode (SHE), a; activity, p; pressure of H₂

Hydrogen reference electrode



http://www.ips-jaisle.de/en/H2REFEL_En.html

Standard Electrode Potential



<http://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0/s23-02-standard-potentials.html>

Standard Electrode Potential (표준전극전위)

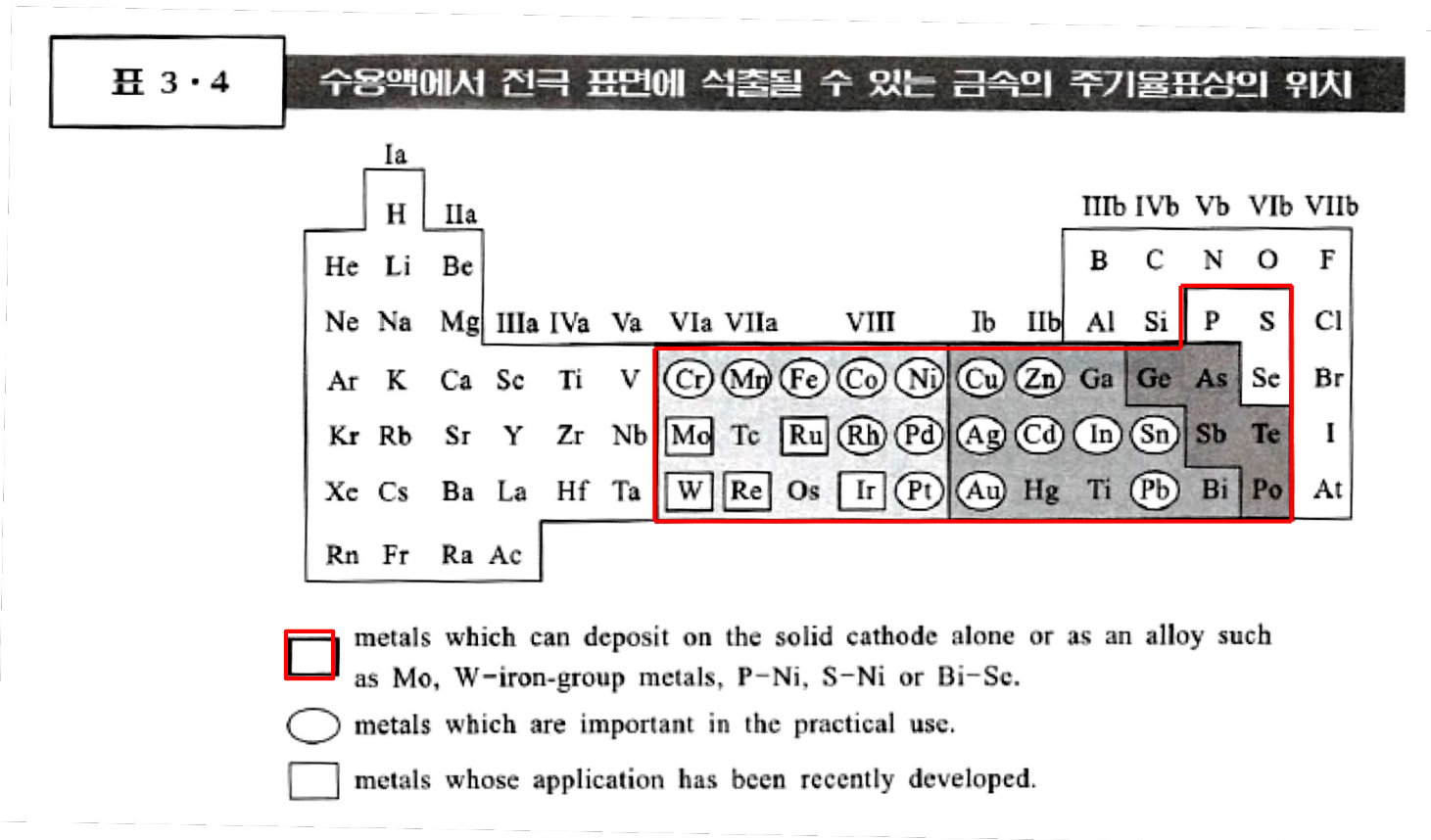
the relative standard electrode potential of Cu, E° ; +0.337V
 → cell potential ; in volts (V), 1 V = 1 joule/coulomb (J/C)

Reaction (Oxidised form + ne ⁻ → Reduced form)	E°/V
$F_2(g) + 2e^- \rightarrow 2F^-$	2.87
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.81
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^- \rightarrow Au(s)$	1.40
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^- \rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^- \rightarrow Ag(s)$	0.80
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68
$I_2 + 2e^- \rightarrow 2I^-$	0.54
$Cu^+ + e^- \rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^- \rightarrow Cu(s)$	0.34
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^- \rightarrow Ag(s) + Br^-$	0.10
$2H^+ + 2e^- \rightarrow H_2(g)$	0.00
$Pb^{2+} + 2e^- \rightarrow Pb(s)$	-0.13
$Sn^{2+} + 2e^- \rightarrow Sn(s)$	-0.14
$Ni^{2+} + 2e^- \rightarrow Ni(s)$	-0.25
$Fe^{2+} + 2e^- \rightarrow Fe(s)$	-0.44
$Cr^{3+} + 3e^- \rightarrow Cr(s)$	-0.74
$Zn^{2+} + 2e^- \rightarrow Zn(s)$	-0.76
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Al^{3+} + 3e^- \rightarrow Al(s)$	-1.66
$Mg^{2+} + 2e^- \rightarrow Mg(s)$	-2.36
$Na^+ + e^- \rightarrow Na(s)$	-2.71
$Ca^{2+} + 2e^- \rightarrow Ca(s)$	-2.87
$K^+ + e^- \rightarrow K(s)$	-2.93
$Li^+ + e^- \rightarrow Li(s)$	-3.05

Half Reaction	potential
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87 V
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.67 V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36 V
$Ag^+ + 1e^- \rightleftharpoons Ag$	+0.80 V
$Fe^{3+} + 1e^- \rightleftharpoons Fe^{2+}$	+0.77 V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34 V
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00 V
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	-0.04 V
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.13 V
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44 V
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76 V
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.66 V
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.36 V
$Li^+ + 1e^- \rightleftharpoons Li$	-3.05 V

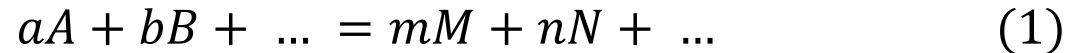
Standard Electrode Potential

- ▶ Non-plating metals from aqueous solutions
; more negative reduction potential of the metal ions than that of solvent and supporting electrolyte



Nernst equation

; concentration dependence of equilibrium cell voltage



free energy change (ΔG) as a function of cell voltage (E)

$$\Delta G = -zFE \quad (2) \quad \text{전위차 (E) 가 크면 } \Delta G \ll 0 \rightarrow \text{반응이 잘 일어남}$$

where, z ; number of electrons involved in the reaction

F ; Faraday number (96,487 C/mol) 1 mole 의 전자가 가지는 총 전하량

E ; the cell voltage

식 (2)의 유도,
electric work, W

$$\begin{aligned} W &= qV & V: \text{the voltage (E)} \\ \Delta G &= -W & W: \text{the work done } (\Delta G) \\ &= -qV & q: \text{total charge (C, zF)} \\ &= -zFE \end{aligned}$$

Nernst equation

Free energy change as a concentration (activity) of the reaction

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (3)$$

$$\text{where, } Q = \frac{a_M^m \cdot a_N^n \cdot \dots}{a_A^a \cdot a_B^b \cdot \dots} = \frac{\Pi[\text{products}]}{\Pi[\text{reactants}]} \quad (4)$$

where, R; the gas constant (8.314 J/mol•K), T; the absolute temperature, Π ; the product of the concentrations (activities, a) raised to the power of their stoichiometric number, Q; reaction quotient (반응지수, 반응물과 생성물 농도 비율)

For standard states, when activities of the reactants and products equal 1

From eq. (2) and (3)

$$\Delta G^\circ = -zFE^\circ \quad (5)$$

Where, ΔG° is the standard free-energy change (모든 농도가 1M)
 E° is the cell voltage for standard states of reactants and products

put eq. (2) and (5) into eq. (3)

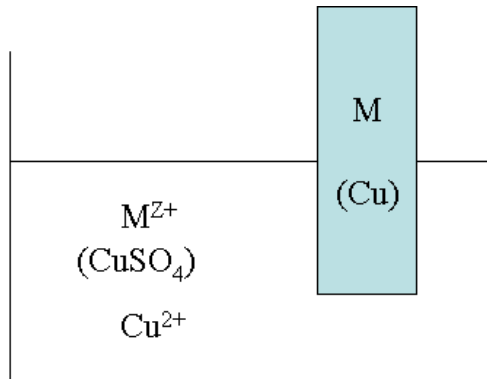
$$-zFE = -zFE^\circ + RT \ln Q \quad (6)$$

$$E = E^\circ - \frac{RT}{zF} \ln Q \quad \text{or} \quad E = E^\circ + \frac{RT}{zF} \ln \frac{1}{Q} \quad (7)$$

$$E = E^\circ + \frac{RT}{zF} \ln \frac{\Pi[\text{reactants}]}{\Pi[\text{products}]} \quad (8)$$

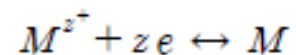
⇒ dependence of the equilibrium cell voltage on the concentration

ex) Metal/Metal-ion (M/M^{z+}) electrode potentials are the results of an exchange of metal ions between metal and electrolyte



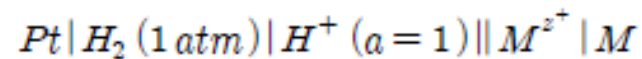
The electrode potential of this electrode depends on the **concentration (more exactly, the activity)** of the metal ions M^{z+} in solution.

The Nernst equation for the concentration dependence of metal/metal-ion potential



reduction reaction consumes electrons

oxidation reaction liberates electrons



From eq. (8)

$$E = E^0 + \frac{RT}{zF} \ln \frac{[M^{z+}][e]^z}{[M]}$$

where, [] is the activity of the species inside the those brackets.

Since the activities of metal(M) and electrons(e) in the metal lattice both equal 1 by convention.

$$E = E^0 + \frac{RT}{zF} \ln [M^{z+}]$$

convert the natural logarithm into decimal logarithm

$$E = E^0 + \frac{RT}{zF} 2.303 \log [M^{z+}]$$

$$\frac{RT}{F} = 0.0257 \text{ V at } 298\text{K (} 25^\circ\text{C)}$$

$$\frac{8.31 \text{ J/mol K} \times 298 \text{ K}}{96487 \text{ C/mol}} = 0.0257 \text{ J/C} = 0.0257 \text{ V}$$

$$\therefore E = E^0 + \frac{0.0592}{z} \log [M^{z+}] \quad (9)$$

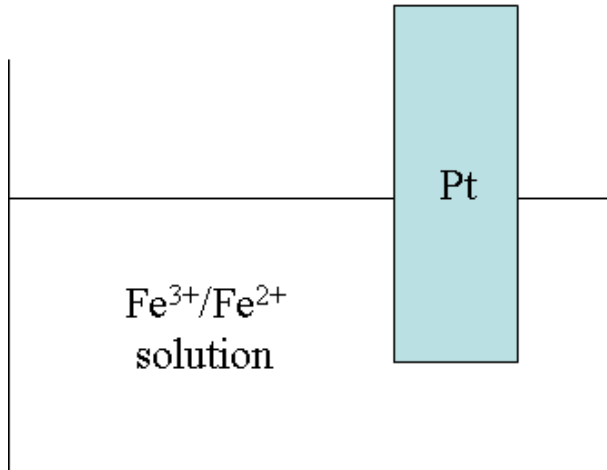
Activity = 1

- 순수한 고체 금속
- 순수한 액체 물
- 순수한 고체 화합물
- 전자

In case of standard state (1atm, 1M)

- 기체
- 용액
- 고체/액체

ex) RedOx (RED/OX) electrode potentials are the result of an exchange of electrons between metal and electrolyte.

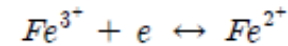


The electrolyte in the RedOx system contain two substances;

- electron donors (electron-donating species)
- electron acceptors (electron-accepting species)

ex) Fe^{3+}/Fe^{2+} RedOx system;

RedOx reaction

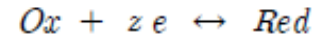


Pt ; the electrode

Fe^{3+} ; the oxidized form

Fe^{2+} ; the reduced form

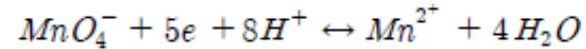
the general RedOx electrode reaction;



where, Ox; the oxidized ions

Red; the reduced ions

ex) Complex RedOx reaction involving H^+



The Nernst equation for concentration dependence of RedOx potential

From eq. (8)

$$E = E^0 + \frac{RT}{zF} \ln \frac{[Ox]}{[Red]}$$

If the activities of the reactants(Ox) and the product(Red) are equal to 1,

$$[Ox]=1, [Red]=1$$

$$E = E^0$$

E^0 ; the standard electrode potential of the RedOx electrode

Kinetics and mechanism of electrodeposition

① Faraday's law for electrolysis

Faraday's law ; the **amount of electrochemical reaction** that occurs at an electrode is proportional to **the quantity of electric charge Q** passed through an electrochemical cell.

$$W = Z \cdot Q \quad (10)$$

where, W ; the weight of a product of electrolysis (g)
Q ; the quantity of electric charge (C)
Z ; the electrochemical equivalent (g/C) **1C 으로 생성되는 물질의 양**

$$Q = I \cdot t \quad (11)$$

where, I ; the current (in amperes, A)
t ; the elapsed time (in seconds, s)

$$\therefore W = Z \cdot I \cdot t \quad (12)$$

* Faraday constant, F ; 96,487 C/mol

Coulomb is **the quantity of electricity transported** by the flow of **one ampere for one second**

$$1C = 1 A \cdot sec$$

$$F = N_A \cdot e = (6.0225 \times 10^{23})(1.6021 \times 10^{-19}) = 96,487 C/mol$$

where, N_A ; Avogadro's number, 6.0225×10^{23} molecules/mol

e ; the charge of a single electron, $1.6021 \times 10^{-19} C$

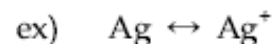
* One equivalent, W_{eq} ; (1그램 당량 – 1몰의 전자와 반응하는 물질의 질량)

Fraction of **a molar (atomic) unit** of reaction that corresponds to the transfer of **one electron**

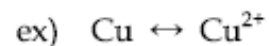
$$W_{eq} = \frac{A_{wt}}{n} \quad (13)$$

where, A_{wt} ; the atomic weight of metal deposited on the cathode

n ; number of electron involved in the electrodeposition reaction



$$\text{for Ag, } W_{eq} = \frac{\text{gram atomic weight of Ag}}{1} = \frac{107.88}{1} = 107.88$$



$$\text{for Cu, } W_{eq} = \frac{\text{gram atomic weight of Cu}}{2} = \frac{63.546}{2}$$

If, $Q = 1$ Coulomb or $Q = 1 \text{ A} \cdot \text{sec}$

$$W_{Q=1} = Z \quad (14)$$

thus, the electrochemical equivalent of a metal M, $Z(M)$, is the weight in grams produced, or consumed, by one coulomb (one ampere second)

$$W = W_{Q=1} \cdot Q \quad (15)$$

Since 96,487 coulombs are required for the electrodeposition of an equivalent of a metal, W_{eq} ,

$$W_{eq} = 96,487 \cdot Z$$

and

$$Z = W_{Q=1} = \frac{W_{eq}}{96,487} = \frac{W_{eq}}{F} \quad (16)$$

From eq. (13) and eq. (16)

$$Z = \frac{A_{wt}/n}{F} = \frac{A_{wt}}{nF} \quad (17)$$

From eq. (10) and eq. (17)

$$W = Z \cdot Q = \frac{A_{wt}}{nF} Q = \frac{A_{wt} \cdot I \cdot t}{nF} \quad (18)$$

$W_{eq} = 1$ 몰의 전자와 반응하는 물질의 양 g/mol
 $Z = 1$ C의 전기량으로 생성되는 물질의 양 g/C
 $F = 1$ 몰의 전자의 전기량 C/mol

Current efficiency

From Faraday's law, the overall amount of chemical change produced by any given quantity of electricity can be exactly accounted for.

the current efficiency, CE

$$CE = \frac{M_a}{M_t} \times 100$$

where M_a ; the actual amount of metal deposited (or dissolved)

M_t ; the theoretically calculated amount of metal from Faraday's law

If all the applied current had been used for depositing the metal to the cathode, it is called the cathode efficiency. (CE = 100%)

- The factors effected on the cathode efficiency
 - electrolyte or bath
 - chemical component concentrations
 - pH
 - Agitation (교반)
 - current density

Current density and distribution

Not uniform thickness from one edge of the cathode to the other from electrodeposition process

⇒ the possible presence of discontinuities in forms of pores, cracks and other irregularities

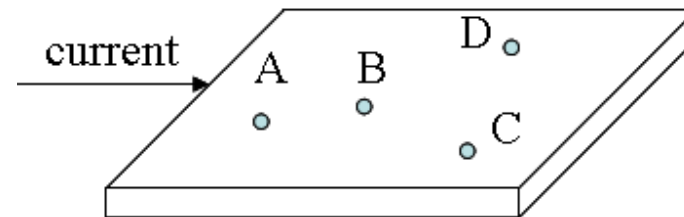
- Definition of current density

$$J = \frac{di}{ds}$$

where, J ; the magnitude of the current density

di ; the element of current impinging on ds

ds ; the element of cathode surface area



The current density over a cathode will vary from point to point.

Current tends **to concentrate** at edges and protruding points. (튀어나온)

Current tends to be **low** in recesses, vias, and cavities. (들어간)

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- Electric field strength ; $E = \frac{V}{L}$

Current tends to flow more readily to points nearer to the opposite electrode than to more distant points.

The thickness of deposit will tend to vary over the surface of the cathode and be thicker at edges and points (bumps)

- * The factors effected on the **uniformity** of deposited metal
 - the shape and dimensions of the object
 - the geometry of the plating cell
 - the conductivity of the bath
 - the shape of polarization curves,
 - CE-current density (or similar) curves
 - the effect of agitation