Lecture Note #13 (Spring, 2022)

Electrodeposition

1. Electroplating
2. Electroless plating
3. Conversion coating
4. Electrophoretic painting
5. Other related surface-finishing techniques

Fuller & Harb (textbook), ch.13, Pletcher & Walsh (ref.), ch. 8, Paunovic, 전체

Electrodeposition

- The reduction and deposition of an electronically conductive species at the cathode of an electrochemical cell
- A shorten form of ‘electrolytic deposition’
- used for depositing metals on surfaces (electroplating, metal finishing) etc

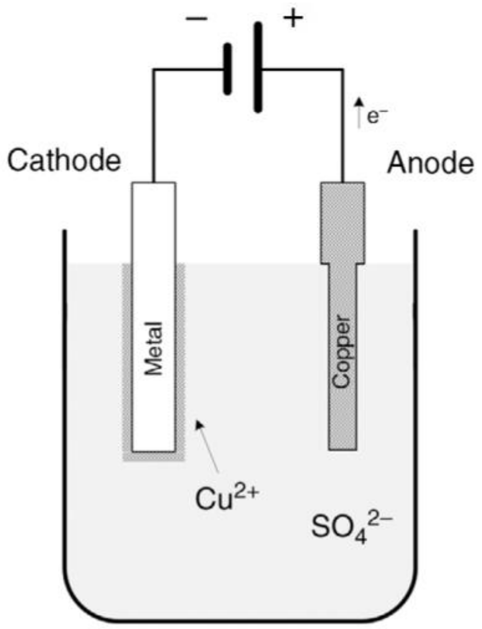

Figure 13.1 Illustration of an electroplating cell with a consumable anode.

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Electroplating (metal finishing)

- To modify the surface properties by the deposition of a layer of another metal or a polymer, or by formation of an oxide film

- To enhance the value by improving their appearance, corrosion resistance, particular physical or mechanical properties to the surface (e.g. electrical conductivity, heat or wear resistance, lubrication or solderability)

- To make possible the use of cheaper substrate metals or plastics covered to give them essential metallic surface properties

- Objects of everyday life (e.g. car components, kitchen utensils, food cans, metal window frames), electronic components (e.g. printed circuit boards, capacitors, contacts)

Electroplating

Substrate and coating metals

- Coating metal: metals(Cu, Sn, Ni, Cr, Zn, Cd, Pb, Ag, Au, Pt) and alloys(Cu-Zn, Cu-Sn, Pb-Sn, Sn-Ni, Ni-Co-Ni-Cr, Ni-Fe), metal-polymer or metal-ceramic composite(metals containing dispersed solids such as PTFE, Al_2O_3, WC, diamond, SiC, Cr_3C_2, graphite)
- Substrate: metal, alloy, polymer, ceramic, composite

Fundamental of electroplating

- To prepare a deposit which adheres well to the substrate and which has mechanical, chemical, and physical properties
- Principle of electroplating
- Essential components of electroplating

(1) Electroplating bath containing a conducting salt, the metal to be plated in a soluble form, a buffer, additives

(2) Cathode to be plated

(3) Anode which may be soluble or insoluble

(4) Inert vessel to contain (1), (2), (3), typically, e.g. steel, rubber-lined steel, polypropylene, PVC, and so on

(5) d.c. electrical power source

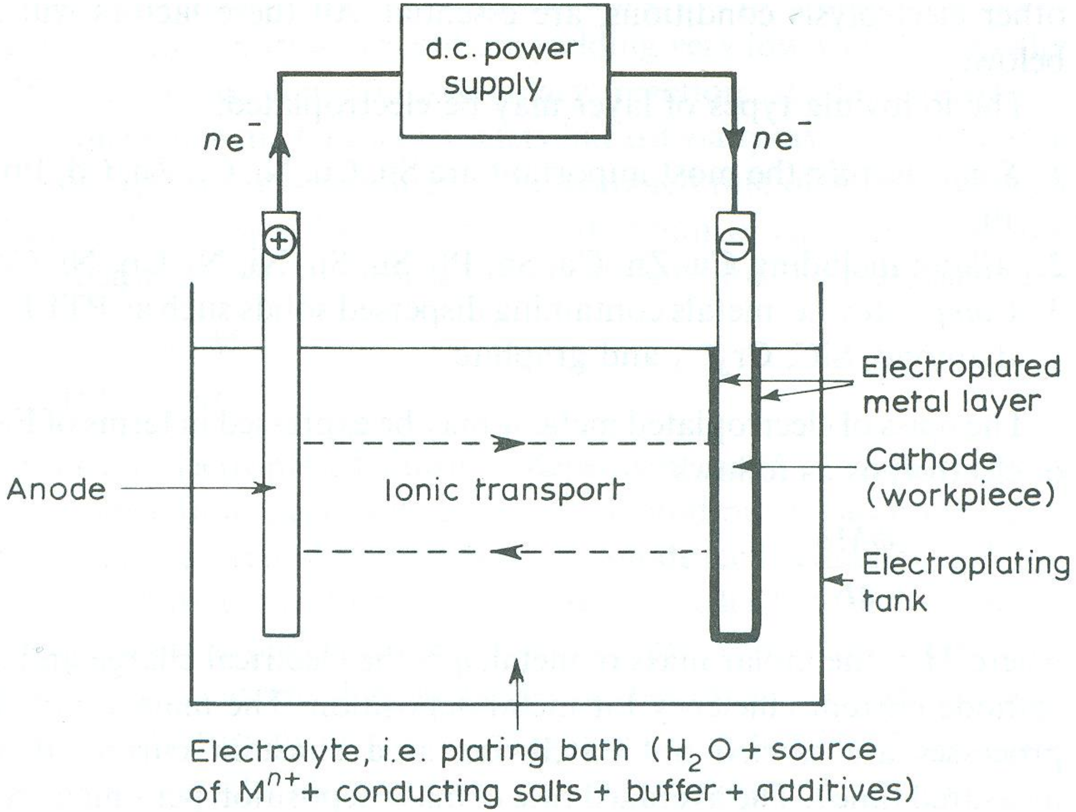


Fig. 8.1 Principle of electroplating.

- Reaction at the cathode, $M^{n+} + ne^- \rightarrow M$
- Anode reaction (in case of the dissolution of the same metal to its precursor in solution), $M \rightarrow M^{n+} + ne^-$

inert anode (insoluble, e.g. platinized titanium (in acid), stainless steel (in alkaline): metal ion has to be added as a salt, a main anode reaction is oxygen evolution

Pletcher, ch.8

Faraday's law and deposit thickness

- total amount deposited is directly related to the amount of charge passed
- Mass of the deposit

$$m_i = M_i Q/nF$$

- Charge passed, Q

$$Q = \int_0^t n_f i A \, dt$$

n_f: the faradaic efficiency for the deposition reaction at cathode

- For constant current density, area, faradaic efficiency

$$Q = n_f i A t = n_f I t$$

- Thickness of the deposited layer, L

$$L = m_i / \rho_i A = M_i n_f I t / \rho_i A n F$$

- Average deposition rate: L/t

Illustration 13.1

cf. Pletcher

- Mass of electroplated metal in terms of Faraday's law of electrolysis

$$w = \frac{\varphi M q}{n\mathrm{F}}$$

M: molar mass of metal, φ(≤1): cathode current efficiency for metal deposition, q: electrical charge, F: Faraday constant (96485 C/mol), *n*: number of electron *n* per mole of M^{n+} → a higher

- Batch process: constant current density I for time t

Average rate of mass deposition per unit area

$$\frac{w}{\mathrm{A}t} = \frac{\varphi I M}{n\mathrm{F}} = \frac{I_M M}{n\mathrm{F}}$$

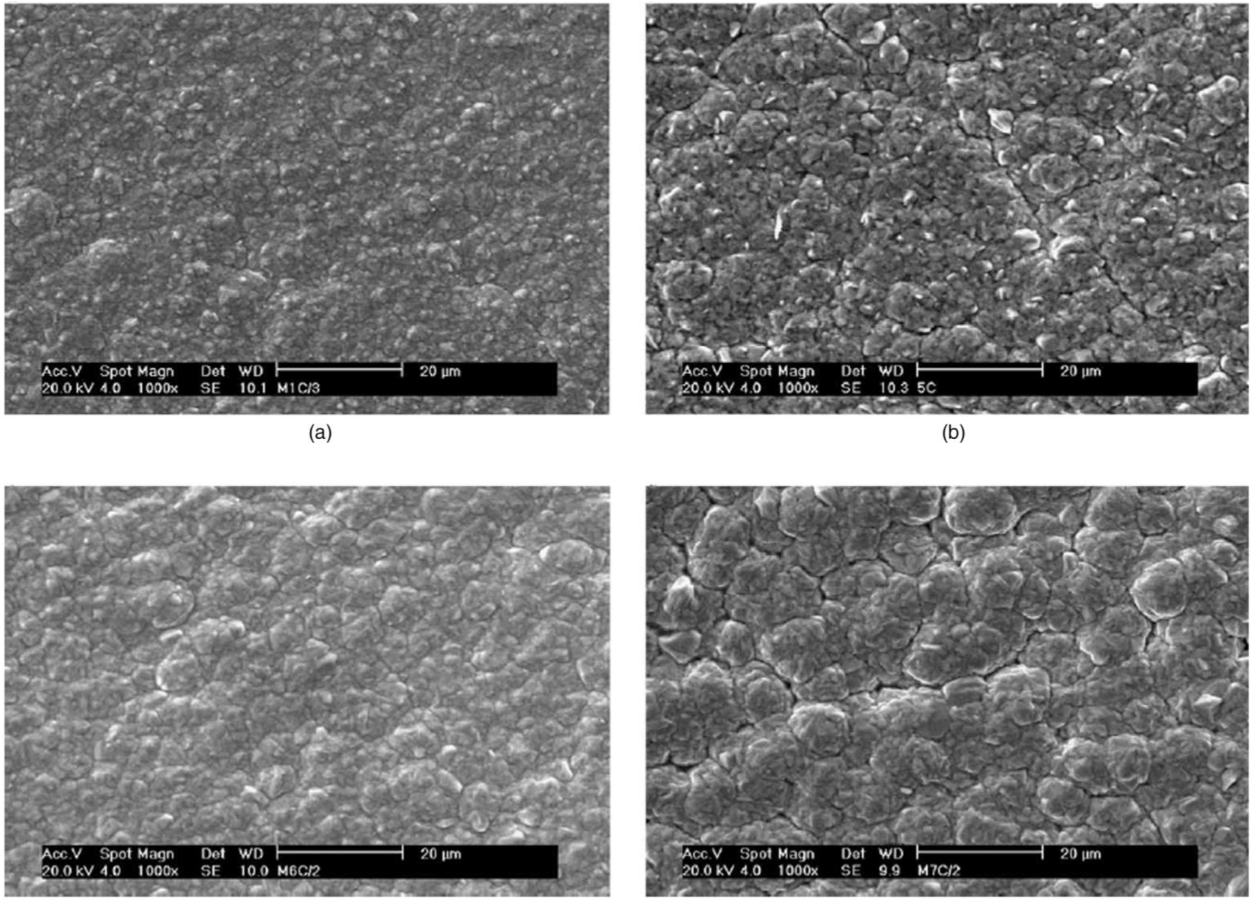
→ rate of deposition ∝ M, 1/n, φ

- Electroplating thickness x, $x/t = \varphi I M / \rho n F$, ρ: mass density
- Cu in acid solution, $Cu^{2+} + 2e^- \rightarrow Cu$
  Cu in alkaline cyanide solution(Cu^{1+}), $[Cu(CN)_2]^+ + e^- \rightarrow Cu + 2CN^-$

- A higher deposition rate for a low oxidation state
- Current efficiency in electroplating baths, 0.9 < φ < 1, excepting Cr deposition from chromic acid (0.05 < φ < 0.20, due to hydrogen evolution)

Electrodeposition fundamentals

- different morphology with different conditions



(a) (b)

(c) (d)

Figure 13.2 Examples of morphologies of copper deposits grown at (a) 60, (b) 1200, (c) 2400, and (d) 5000 $A \cdot m^{-2}$. (From A. Ibañez and E. Fatás (2005) *Surface & Coatings Technology*, **191**, 7–16. Reprinted with permission from Elsevier.)

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- Real surfaces have a variety of defects

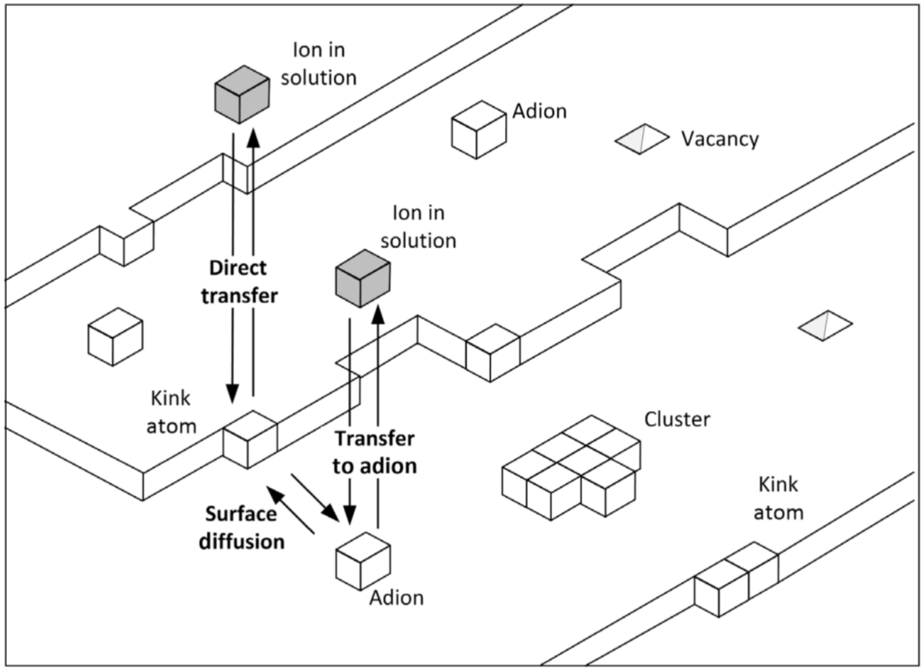

Figure 13.3 Schematic diagram of the structure of a crystal face with a simple cubic lattice. *Source:* Adapted from Budevski 1996.

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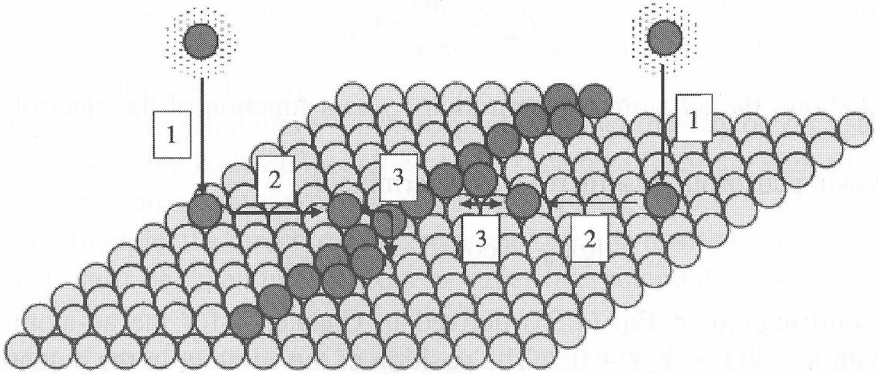

Figure 7.10 Model of an electrochemical deposition process: (1) charge transfer of an ion in the electrolyte to an ad-atom position, (2) surface diffusion of ad-atoms, and (3) transfer of an ad-atom into a step or kink position.

Plieth

- e.g. growth in dislocation defects : deposition can continue in a spiral form

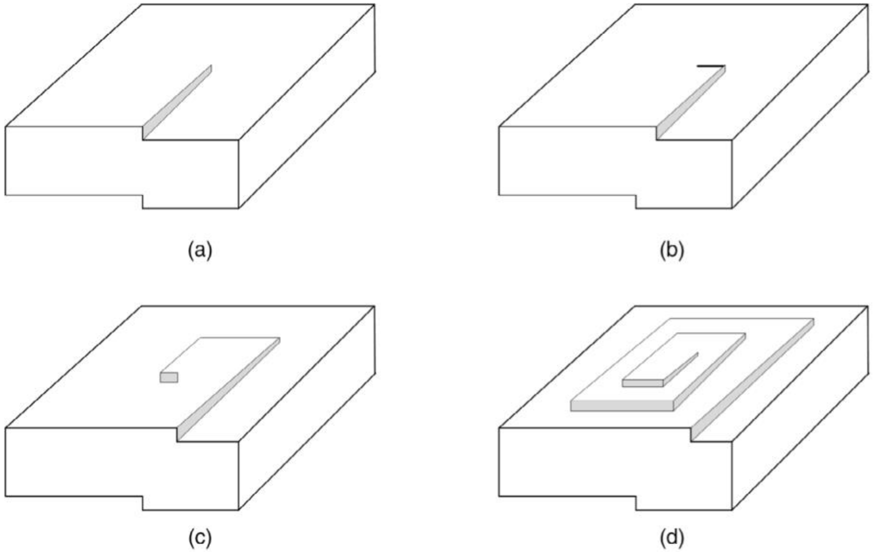

Figure 13.4 Spiral growth around a screw dislocation during deposition of a metal.

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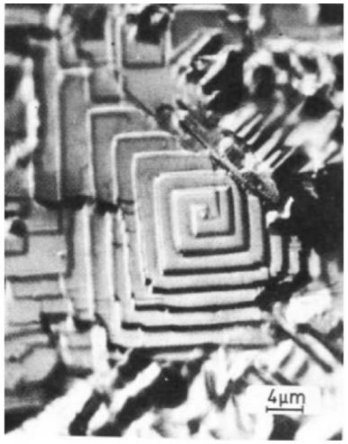

Figure 13.5 Crystallographic copper deposit showing macro-spiral growth. *Source:* Reproduced with permission of German Bunsen Society.

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Formation of stable nuclei

- Nucleation : the formation of new sites or nuclei from which deposition may occur, and it is a critical aspect of electrodeposition
- Gibbs energy of cluster formation of N atoms

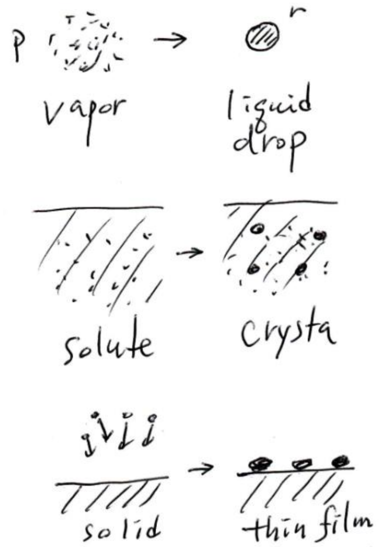
$$\Delta G(N) = -Nzq|\eta_s| + \varphi(N)$$

1st term: the change in the electron energy due to the difference in potential between the metal and the solution. Always negative under deposition

2nd term ($\varphi(N)$): the excess energy associated with the formation of cluster. Always positive

cf: Formation of a new phase : nucleation and crystal growth

vapor → liquid drop
solute in a liquid → crystal



- In the initial stage of condensation a liquid drop of radius r is formed from a supersaturates vapor
- Small drop has a high vapor pressure → it tends to re-evaporate →
- Therefore, only droplets of a radius greater than a critical radius r_c (embryo) survive and grow.
- This process is called nucleation and the nuclei grow in time.

Consider the free energy change in nucleation of a droplet from a vapor.

nA (gas,P) → A_n (small liquid drop, r)

$$\Delta G = -nRT \ln(P/P_o) + 4\pi r^2\gamma$$
$$= -(4/3)\pi r^3(\rho/M)RT \ln(P/P_o) + 4\pi r^2\gamma$$

M= molecular weight, ρ = density
P_0 = equilibrium vapor pressure
P/P_0 = degree of supersaturation

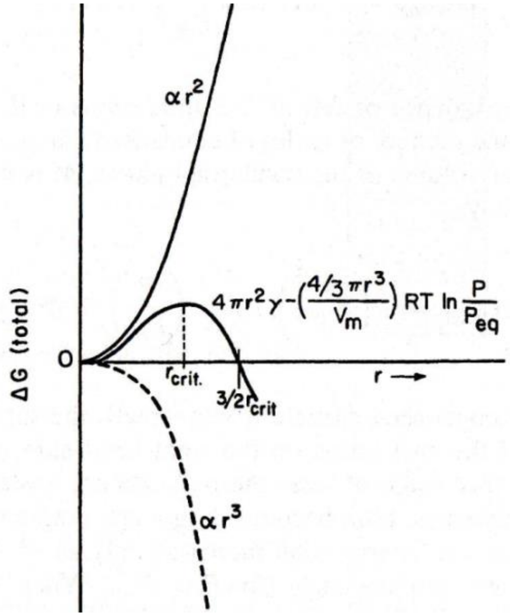
$$\boxed{\begin{array}{l} d(\Delta G)/dr = 0 \quad \text{at } r = r_c \\ r_c = 2\gamma V_m / RT \ln(P/P_o) \end{array}}$$

for sphere

This means there is always a free energy barrier of

$$\Delta G_m = 16\,\pi\,\gamma^3\,V_m /3\,[RT \ln (P/P_0)]^2$$

which is overcome by thermal fluctuation.



* Related concepts

artificial raining: spraying dry ice particle in the damp air
seeding in crystallization: adding a crystal seeds in a supersaturated solution

cf: Nucleation theory

-The change in Gibbs energy upon forming a spherical cluster or droplet of radius r from N atoms (or molecules)

$$\Delta G = -N\ \Delta\mu + 4\pi r^2 \gamma \qquad (7.5.1)$$

→ chemical potential change brought about by the phase transformation of N atoms into a sphere with a surface energy given by the 2nd term

-Number of atom in the clusters and the radius are related by

$$N = \frac{4\pi}{3}\frac{r^3 N_A \rho}{M} = \frac{4\pi}{3} r^3 \overline{\rho}, \qquad (7.5.2)$$

where N_A is the Avogadro constant, ρ the mass density, M the molar mass, and $\overline{\rho}$ the number density.

-Combining (7.5.1) and (7.5.2) and differentiating with respect to either N or r → values for the size of critical classical nucleus

$$N_c = \frac{32\,\pi\gamma^3}{3\overline{\rho}^2 \Delta\mu^3} \quad \text{and} \quad r_c = \frac{2\gamma}{\overline{\rho}\Delta\mu}$$

for sphere

-Critical radius r_c → the smallest structure for which the probability of growth is greater than that of decay

-r_c →(7.5.1) → energy barrier to nucleation

$$\Delta_{\max} G = \frac{4\pi r_c^2 \gamma}{3}$$

3-dimensional nucleation

$$\varphi(N) = A_s\gamma$$

A_s: surface area of the 3D crystal, γ: average specific surface energy (Jm^{-2})

-Volume of cluster, $V = V_mN$, V_m: the volume of one atom in the lattice

$$A_s^3 = BV^2 \qquad \text{(for spherical shape, } B = 36\pi\text{)}$$

$$\varphi(N) = A\gamma = B^{1/3}V^{2/3}\gamma = (B^{1/3}V_m^{2/3}\gamma)N^{2/3}$$

Gibbs energy of cluster formation of N atoms in 3D

$$\Delta G(N) = -Nzq|\eta_s| + (B^{1/3}V_m^{2/3}\gamma)N^{2/3} \qquad (13.8)$$

Illustration 13.2

Fig. 13.6

- surface energy term (φ(N)) is positive

And dominates at low N

-first term is negative and dominates

At high N

→ ΔG(N) has a maximum at a particular

N → N_{crit}

- Cluster size > N_{crit} →
  spontaneous growth

-Two different overpotentials:

At higher η_s → lower N_{crit}

(increasing overpotential →

stable growth from smaller seed

clusters) → nucleation is favored

at higher overpotential

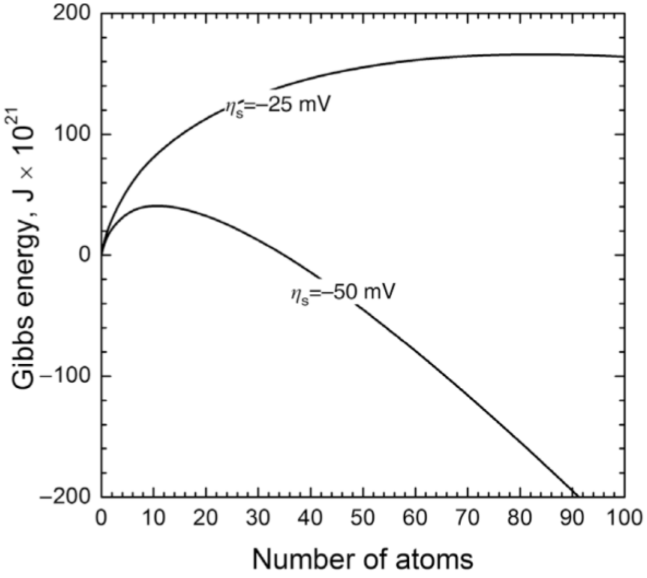


Figure 13.6 Gibbs energy of cluster formation as a function of the number of atoms in the cluster. *Parameters:* Ag atom (0.1444 nm radius), $\gamma = 0.1\ \mathrm{J{\cdot}m^{-2}}$, $z = 1$, atoms and clusters assumed spherical.

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- differentiating (13.8) & setting zero,

→ in Fig. 13.6, N_{crit} = 83 and 10 atoms

- Gibbs energy of cluster formation at N_{crit}

$$N_{crit,3D} = (8BV_m^2\gamma^3) / 27(zq|\eta_s|)^3$$

$$\Delta G_{crit,3D} = (4BV_m^2\gamma^3) / 27(zq|\eta_s|)^2 = (N_{crit}zq|\eta_s|) / 2 \qquad (13.10)$$

Illustration 13.3

2-dimensional nucleation

In 2D, surface area → perimeter (P)

$$\varphi(N) = P\varepsilon$$

ε: average specific edge energy (Jm^{-2})

-Area of cluster, $A_s = \Omega N$, Ω: the area of one atom on the surface
→ $P^2 = 4bA_s$, b: constant of proportionality

$$\varphi(N) = P\varepsilon = 2\varepsilon(b\Omega N)^{1/2}$$

Gibbs energy of cluster formation of N atoms in 2D

$$\Delta G(N) = -Nzq|\eta_s| + 2\varepsilon(b\Omega N)^{1/2} \quad (13.13)$$

$$N_{crit,2D} = (b\Omega\varepsilon^2) / (zq|\eta_s|)^2$$

$$\Delta G_{crit,2D} = (b\Omega\varepsilon^2) / (zq|\eta_s|) = N_{crit}zq|\eta_s| \quad (13.15)$$

- 2D growth → 2D monoatomic layers → UPD (underpotential deposition)

UPD (underpotential deposition)

- 2D deposition at potential below that needed for sustainable deposition onto a native metal substrate

1. Overpotential deposition, OPD:

$$E < E(\mathrm{M/M}^{n+}), \qquad \Delta E < 0$$

2. Underpotential deposition, UPD:

$$E > E(\mathrm{M/M}^{n+}), \qquad \Delta E > 0$$

One interesting example of UPD deposition is deposition of Cu on Au(111) substrate. Figure 7.21*b* shows a cyclic voltammogram of Cu–UPD on Au(111) substrate, and Figure 7.21*a* shows a cyclic voltammogram of Au(111) electrode

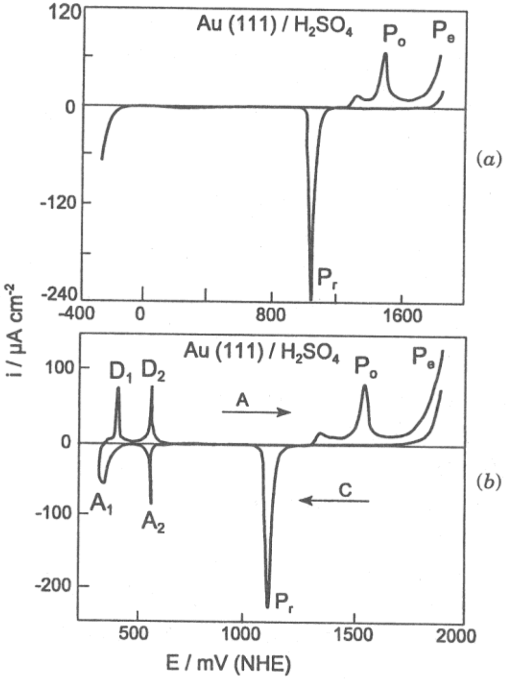

Figure 7.21. Cyclic voltammograms of Au(111) electrode in 9.10^{-2} M H_2SO_4, (top) absence of Cu^{2+} ions, and presence of Cu^{2+} ions, 10^{-2} M $CuSO_4$ (bottom). (From Ref. 40, with permission from the ELectrochemical Society.)

Paunovic. Schlesinger

UPD

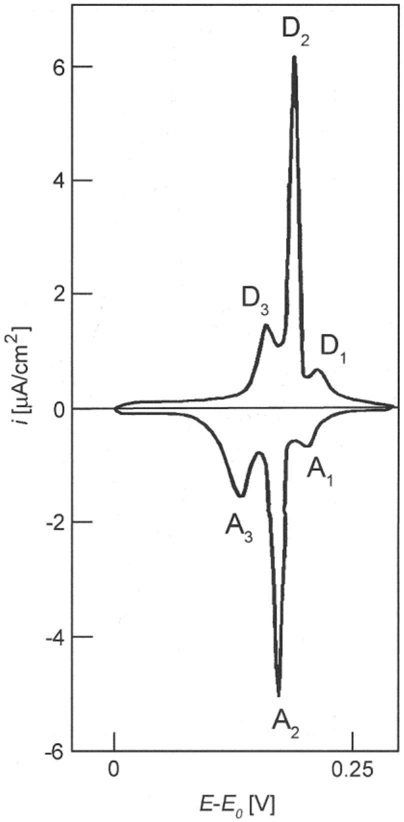

Figure 4.27 Cyclic voltammogram of UPD of lead on a Ag(111) surface.[60] The reference potential E_0 is the Nernst potential of a lead/lead ion electrode in the same solution. 5×10^{-4} mol·dm^{-3} $Pb(ClO_4)_2 + 5 \times 10^{-1}$ mol·dm^{-3} $NaClO_4$ + 5×10^{-3} mol·dm^{-3} $HClO_4$, 25 °C. Scan rate 0.42 mV·s^{-1}. (Reproduced with permission from Ref. [60], © 1978, Elsevier.)

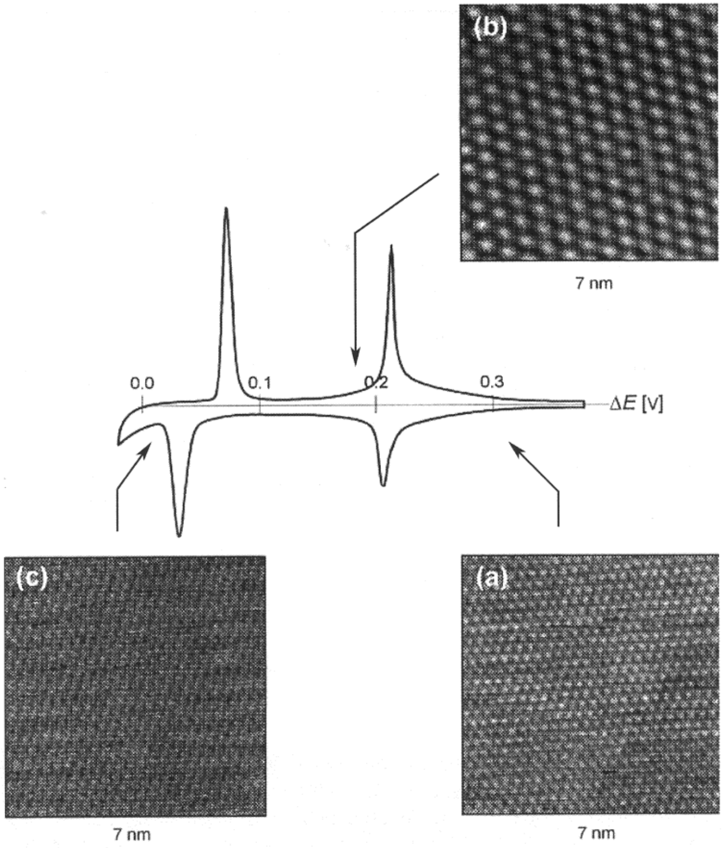

Figure 4.33 Cyclic voltammogram of UPD of copper on a Au(111) surface.[63] STM images at different potentials of the CV. 10^{-3} mol · dm^{-3} $CuSO_4 + 5 \times 10^{-2}$ mol · dm^{-3} H_2SO_4, 25 °C. (Reproduced with permission from Ref. [63], © 1995, Kluwer Academic Publishers.)

Plieth

Cu UPD on Au(111) & Pt(111)

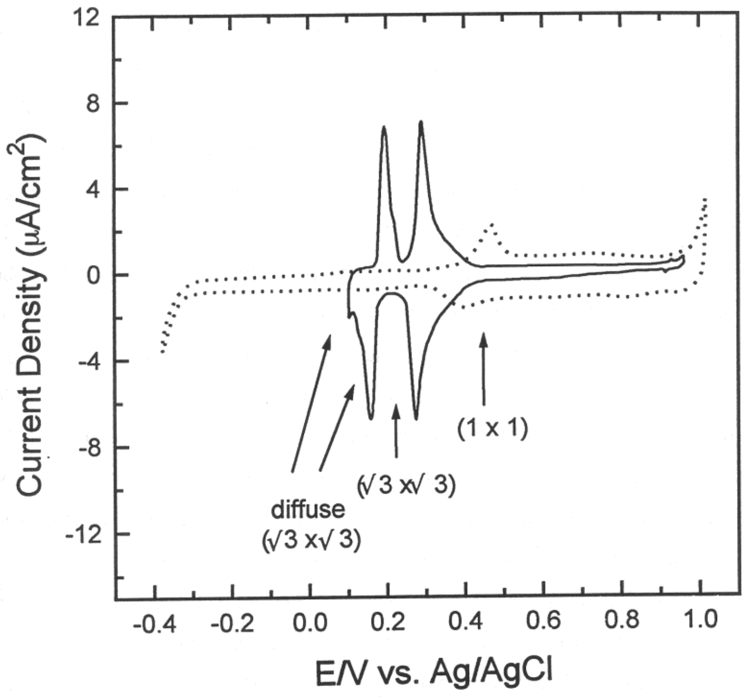

Figure 6.1 Cyclic voltammetry of Au(111) electrode before (dotted line, at 10 mV/s) and after (solid line, at 2 mV/s) addition of 1 mM $CuSO_4$ in 0.1 mM sulfuric acid solution. Scan rates are shown in the plot. The corresponding LEED structures are assigned at each potential region.

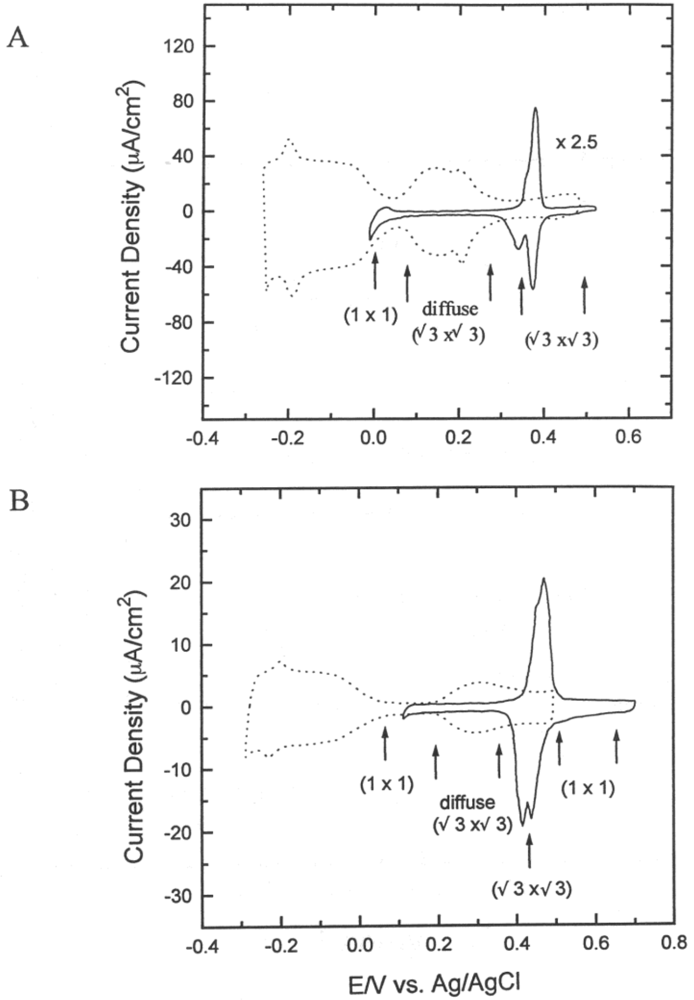

Figure 6.6 Cyclic voltammetry of Pt(111) electrode before (dotted line) and after (solid line) addition of 1 mM $CuSO_4$ in sulfuric acid solution. Concentrations of sulfuric acid are (A) 50 mM, and (B) 0.1 mM. Scan rates are 50 mV/s, 10 mV/s in 50 mM and 0.1 mM sulfuric acid solution, respectively, and 2 mV/s for UPD CV.

Sung, Ph.D thesis

Nucleation rates

-Nucleation rate, J ($cm^{-2}\cdot s^{-1}$) : rate per area of nuclei formed on the surface

$$J = A_0 \exp(-\Delta G_{crit}/kT)$$

- For 3D, $J = A_{3D} \exp[-(4BV_m^2\gamma^3) / 27(zq|\eta_s|)^2kT]$
- For 2D, $J = A_{2D} \exp[-(b\Omega\varepsilon^2) / (zq|\eta_s|kT)]$

- Nucleation rate vs. overpotential :

rapidly J↑ over narrow range
(in Fig. -0.080 to -0.105 V)
→ $|\eta_{crit}|$ (at J = 1 ($1\ cm^{-2}\cdot s^{-1}$))

J ~ 0 at low overpotentials

value of the overpotential at which the nucleation rate rises sharply

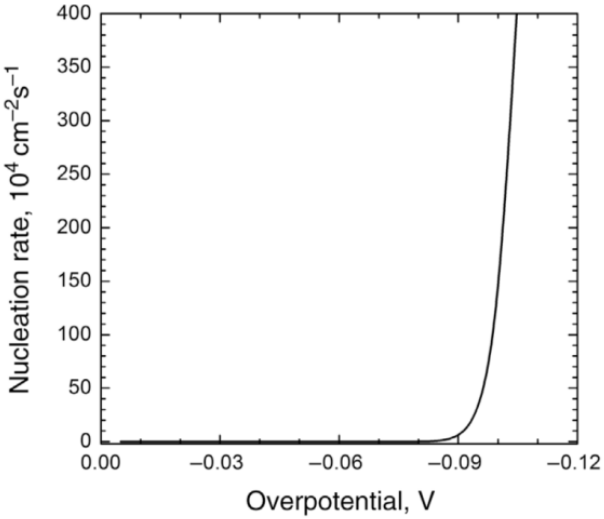

Figure 13.7 The rate of nucleation as a function of overpotential showing the strong dependence on the overpotential.

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- Given that J does not change with time → number of nuclei per area (Z_{nucl}) increases linearly with time (Fig. 13.8)

$$J = dZ_{nucl} / dt$$

-For 3D, J vs. $1/\eta_s^2$ (Fig. 13.9)

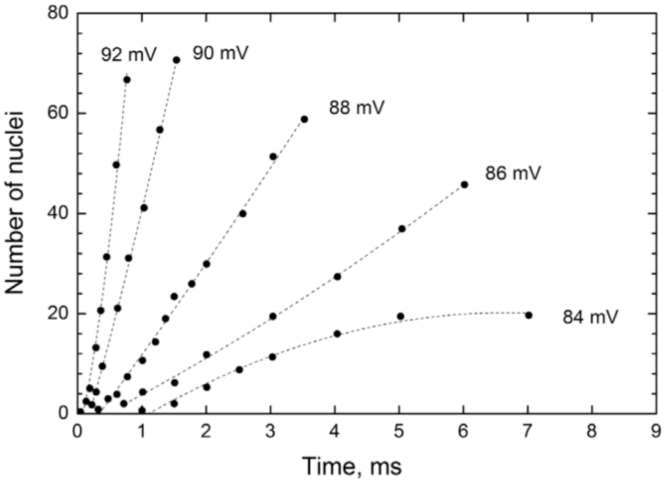

Figure 13.8 The number of nuclei versus time for electrodeposition of mercury on Pt at different overpotentials. *Source:* Adapted from Toshev 1969.

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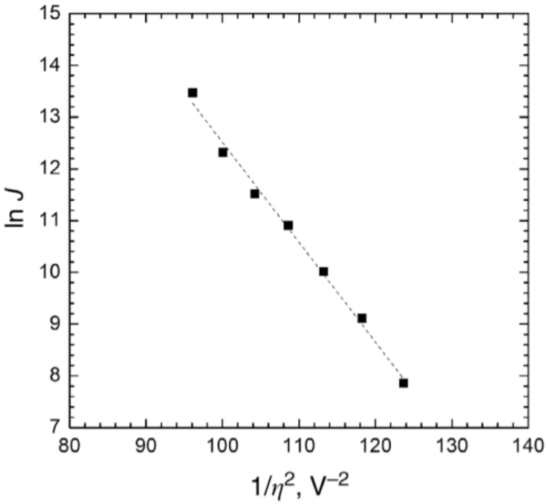

3-D

Figure 13.9 Determination of ΔG_{crit} from a plot of $\ln J$ versus $1/\eta^2$.

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N_{crit} can be estimated,

2-D

$$d \ln J / d|\eta| = -(1/kT)(d\Delta G_{crit} / d|\eta|) = N_{crit}(zq / kT) = N_{crit}(zF / RT)$$

Illustration 13.4

Deposit morphology

- Deposition process has two phases:

(1) Initial stage: in starting process, metal deposition occur on an electrode surface of a different material → 1st step: formation of nuclei of the new phase and their growth into crystals with the characteristic lattice of the electroplating metal → the electrode is fully covered by a few atomic layers of this metal → influence interface adhesion & the structure

(2) Macroscopic deposit: dealing with M/M^{n+} and the thickening of the layer into a macroscopic deposit.

- 3 steps of phase growth in nucleation and early stage: (1) mass transport in solution (diffusion, convection, migration) of the metal-bearing species to the electrode surface, (2) electron transfer to form an adatom, (3) diffusion of the adatom across the surface into a position in the lattice → key parameter is the current density

Pletcher, ch.8

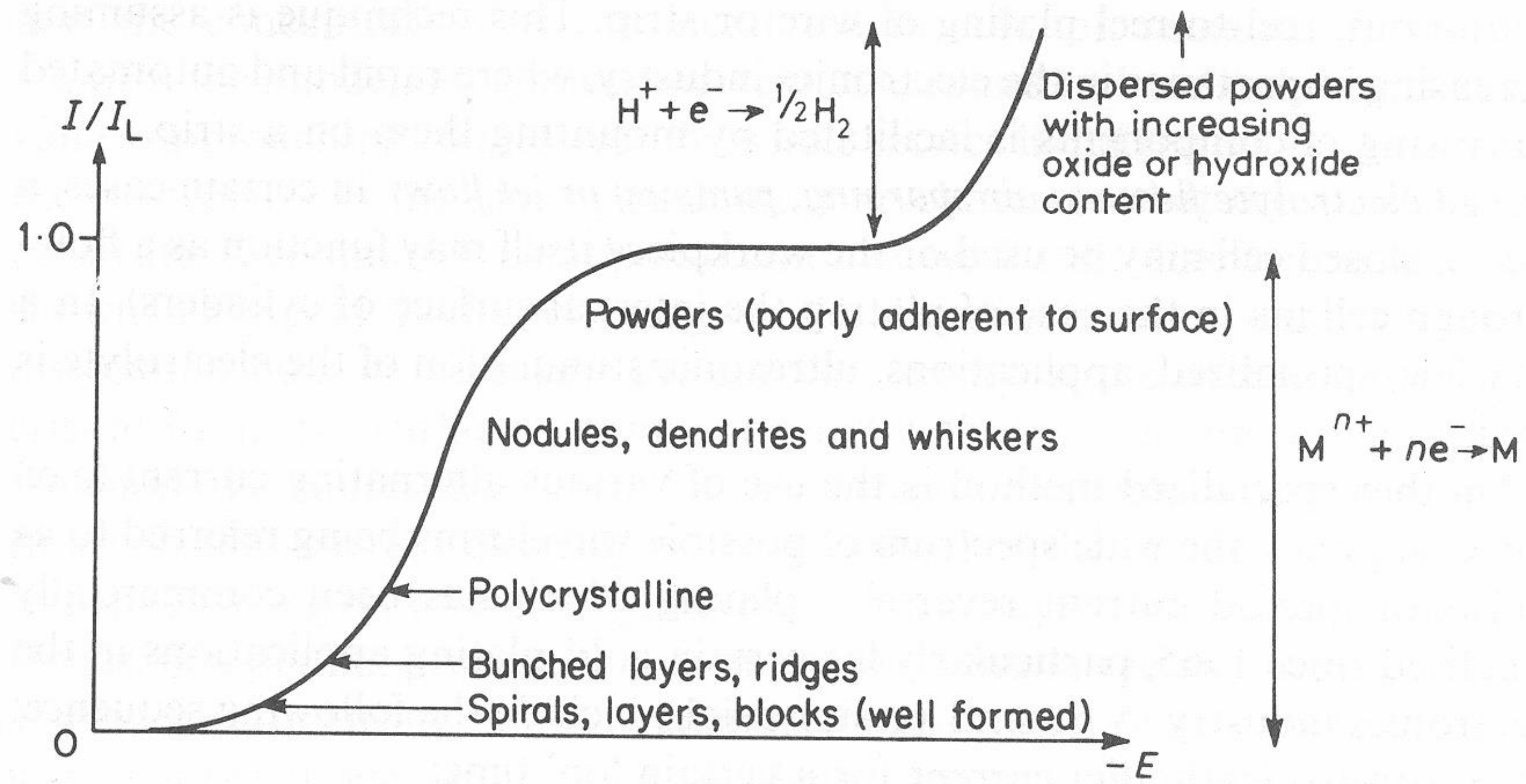

Fig. 8.10 The variation of characteristic growth modes with normalized current density I/I_L.

Keep the plating speed (current) low to improve the quality of the plating layer. Under the condition of low current, the metal of the electrodeposition layer has excellent crystallinity, but when the current is high, it is plated in a dendrite or powder state or cannot be strongly bound to the surface.

도금층의 질을 높이기 위해 도금속도(전류)를 작게 유지. 전류가 작은 조건에서서는 전착층의 금속이 우수한 결정성을 가지나 전류가 크면 침상(dendrite) 혹은 분말 상태로 도금되거나 표면에 강하게 결착하지 못함

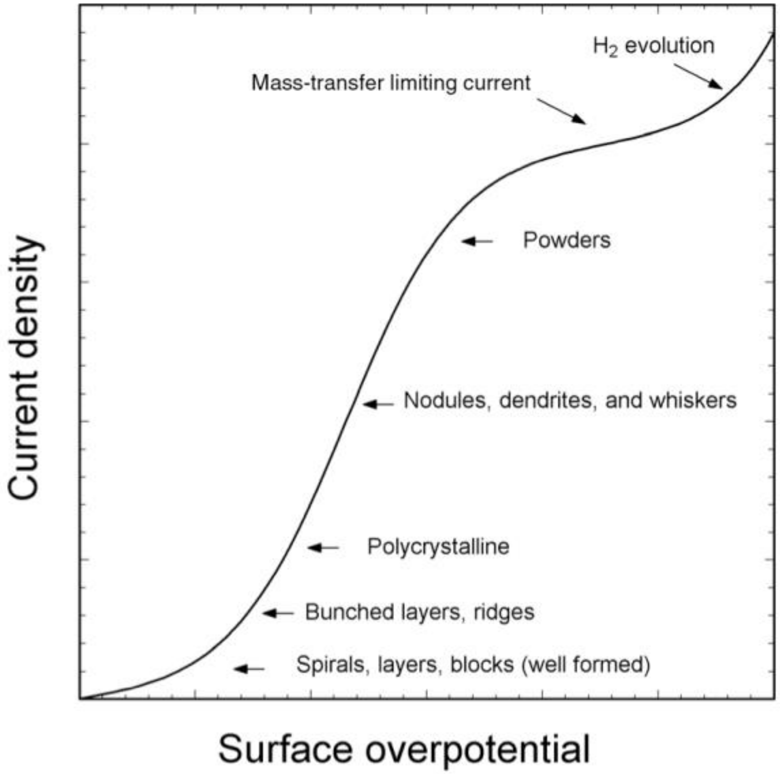

Figure 13.11 Generalization of deposit morphology as a function of overpotential and current. *Source:* Adapted from Pletcher and Walsh.

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Anodes

- Anode is made from the same metal as that being plated at the cathode and condition is selected that the concentration of the metal ion in solution remains constant
- Anode and cathode current efficiencies to be matched
- From Fig. 8.11, in a plating process, it is essential to maintain the anode potential in the active region to ensure smooth and uniform dissolution (maintaining a suitable low current density)
- Additions of complexing agents (preventing passivation) or halide ions (causing pitting of the oxide film)

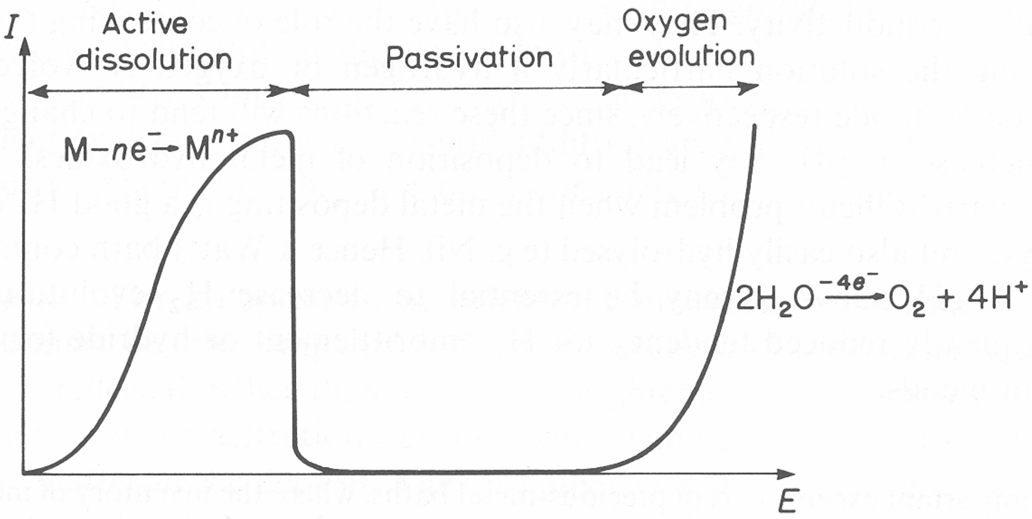


Fig. 8.11 Typical current-potential curve for an anode in an electroplating bath.

Some metals (eg Cr) are passivated when used as an anode and cannot be eluted. Metal ions are generated by dissolving the salt of the metal to be electrodeposited in the electrolyte.

일부 금속(예, Cr)은 산화전극(anode)으로 사용할 경우 부동화(passivation)되어 용출이 불가능. 전착하고자 하는 금속의 염을 전해액에 용해하여 금속 이온 생성시킴

Pletcher, ch.8

Additives

Plating bath

(a) The metal ion: simple hydrated ions or a complex. A non-complexing medium is used for rapid plating on objects of simple shape. Complexing media are employed when a high power is important

(b) Electrolytes: to give the bath maximum conductivity, control pH and buffering the solution (by hydrogen or oxygen evolution) (pH↑ → deposition of metal hydroxides (e.g. Ni))

(c) Complexing agents: to prevent a spontaneous chemical reaction between the cathode and the plating ions
e.g. Cu plating onto iron or steel, $Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}$ reaction
→ cause very poor Cu deposit (porous & badly adherent)

→ a complexing agent is added to make the potential of the Cu^{2+}/Cu couple negative to that of Fe^{2+}/Fe couple (to make the potential more negative), and to modify the Tafel slope for the metal ion reduction to improve the power of the bath (Fig. 8.4)

-Complexing agents: cyanide, hydroxide, sulphamate ion

Nernst equation

E obtained from the Nernst equation

$oO + \mathbf{ne^-} = rR$ (reduction)
$pP = qQ + \mathbf{ne^-}$ (oxidation)
$oO + pP = qQ + rR$ E_{cell} (cell reaction)

$$E_{cell} = E^0 - \left(\frac{RT}{nF}\right)\frac{a_Q{}^q a_R{}^r}{a_O{}^o a_P{}^p}$$

a: activity
activity term: minor contribution to the cell voltage

<u>activity</u> (a) → concentration (c); a = γc, γ; activity coefficient
$a_i \cong 1$(solvent, pure solid, ideal solution)

Metal complex(금속착물): standard electrode potential

$Co^{3+} + e = Co^{2+}$ $E^0 = 1.92$ V (*vs.* NHE)

$Co(NH_3)_6^{3+} + e = Co(NH_3)_6^{2+}$ $E^0 = 0.06$ V (*vs.* NHE) ($E^0_{complex}$)

$Au^{3+} + 3e = Au$ $E^0 = 1.50$ V (*vs.* NHE)

$AuCl_4^- + 3e = Au + 4Cl^-$ $E^0 = 1.00$ V (*vs.* NHE) ($E^0_{complex}$)

$Au^{3+} + 4Cl^- = AuCl_4^-$

$K_f = a_{AuCl4-} / a_{Au3+} \cdot a_{Cl-}^4$

$$E_{eq} = E^0 + \frac{RT}{3F}\ln a_{Au^{3+}} = E^0 + \frac{RT}{3F}\ln\left(\frac{a_{AuCl_4^-}}{K_f a_{Cl^-}^4}\right)$$

$$= E^0 + \frac{RT}{3F}\ln\left(\frac{1}{K_f}\right) + \frac{RT}{3F}\ln\left(\frac{a_{AuCl_4^-}}{a_{Cl^-}^4}\right)$$

$$E^0_{complex} = E^0 + \frac{RT}{3F}\ln\left(\frac{1}{K_f}\right)$$

$$E_{eq} = E^0_{complex} + \frac{RT}{3F}\ln\left(\frac{a_{AuCl_4^-}}{a_{Cl^-}^4}\right)$$

K_f↑(more complex formation)

→ more negative $E_{complex}^0$

→ reducing property↓

Plating bath

(d) Organic additives: to modify the structure, morphology, properties of the deposit.

-Brighteners: to reflect (not scatter) by low microscopic roughness

e.g. Ni deposition: two types of brighteners (i) aromatic sulphones or sulphonates leading to bright deposits (ii) molecule containing -CN, -NCS, >CO (e.g. thiourea, coumarin). Aromatic sulphonates are also brighteners for Sn or Cu

-Levellers: to produce a level deposit on a more macroscopic scale and act by adsorption at points for peaks

-Structure modifiers: to change the structure of the deposit (preferred orientation) or to adjust the stress (due to lattice misfit) ‘stress relievers’

-Wetting agents: to accelerate the release of hydrogen gas bubbles from the surface (to prevent hydrogen embrittlement)

Table 13.1 Examples of Industrial Plating Baths and Conditions

Metal	Electrolyte composition [kg·m^3]	T [°C]	Current density [A·m^{-2}]	Additives	Anode	Current efficiency (%)
Cu	$CuSO_4$ (200–250) H_2SO_4 (25–50)	20–40	200–500	Dextrin, gelatin, S-containing brighteners, sulfonic acids	P-containing rolled Cu	95–99
Ni	$NiSO_4$ (250) $NiCl_2$ (45) H_3BO_3 (30) pH 4–5	40–70	200–500	Coumarin, saccharin, benzenesulfonamide, acetylene derivatives	Ni pellets or pieces	95
Zn	ZnO (20–40) NaCN (60–120) NaOH (60–100)	15–30	100–400	Glycerin, organic additives	Zn	70–90

Source: Adapted from Pletcher 1993.

Impact of current distribution

Current distribution and Wagner number

- Uniformity of the current distribution is characterized by the Wagner number (Wa)

$Wa = (RT\kappa/FL_c)(1/|i_{avg}|\alpha_c)$ (from Butler-Volmer equation)

or

$Wa = (d\eta/di) / (L/\kappa)$ (from Oh, ch.11)

$d\eta/di$: activation overpotential (**활성화과전압**), κ: ionic conductivity

- Higher Wa: more uniform current distribution

A measure of the uniformity of the current density, $Wa = R_{ct} / R_{\Omega}$

Electroplating in the electronic industry

(1) Printed circuit board (PCB)
(2) Electrical contacts and connectors

Overall plating process and the importance of component design

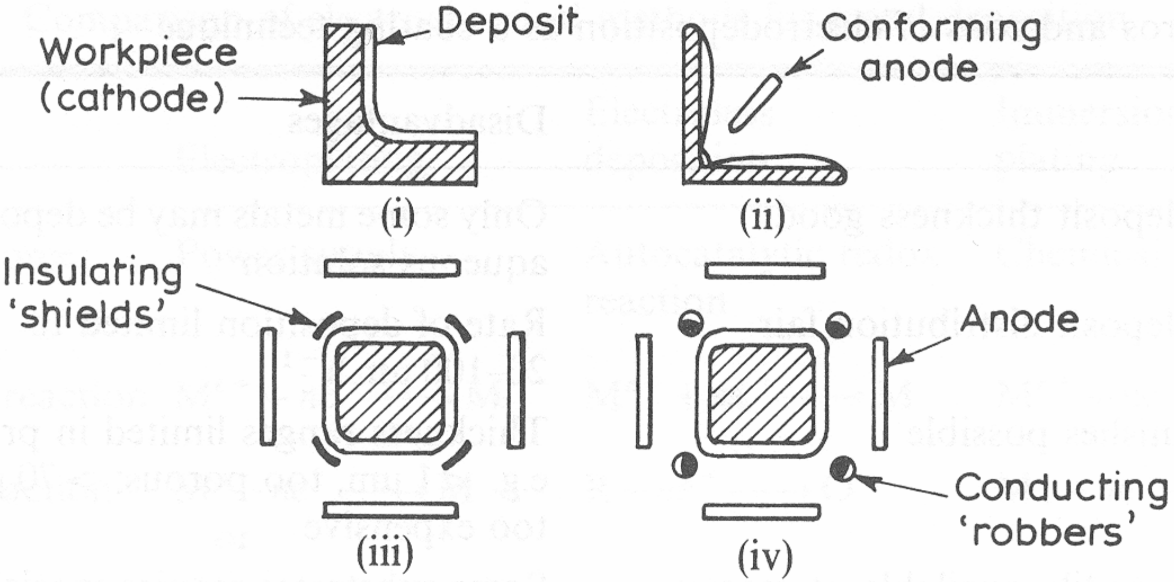


Fig. 8.18 Modification of extreme current densities to provide a more uniform current distribution. (i) use of a radiused corner to reduce throwing power deficiency in a recess; (ii) use of a conforming anode to overcome poor throwing power in a recess; (iii) use of inert shields to prevent build-up of deposits on edges; and (iv) use of cathodic 'burners' or 'robbers' to minimize edge build-up. (After: Ashby (1982) *Electroplating for Engineering Technicians*, National Physical Laboratory, London; and Courtesy: Ionic Plating Ltd.)

Pletcher, ch.8

Throwing power (균일 전착성)

- Good throwing power: ‘uniform’ plating cathode

- T(% throwing power) = 100(K - B)/[K + B -2]

K = x_1/x_2, B = w_2/w_1,
x: distance, w: weight of metal deposited
If current efficiency ~ 100%, $w_2/w_1 \sim i_2/i_1$

T = +100: very good, -100: very poor

e.g. Cr, T < 0, Ni ~0, cyanide complex bath 40~60

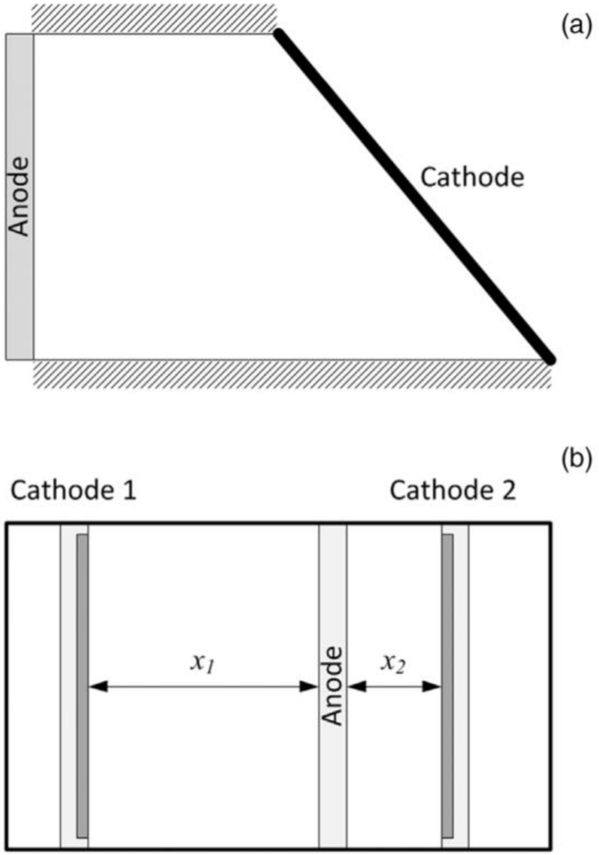


Figure 13.13 Cells for experimental examination of current distribution. (a) Hull cell. (b) Haring–Blum cell.

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

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

Impact of side reactions

- Factors which determine the power of a electroplating bath

(1) Conductivity of the electrolyte: a high conductivity to minimize iR drop so cause uniform deposition

(2) Tafel slope for the deposition reaction: smaller deposition rate in higher Tafel slope ((ii) in Fig. 8.4(a)). Higher Tafel slope when complexing agents and additives are present (which adsorb on the cathode)

(3) Competing electrode reactions

When a strong complex of metal ions and ligands is formed, or when hydrogen is generated, the current decreases and plating occurs at a slow rate, improving the quality of the plating layer.

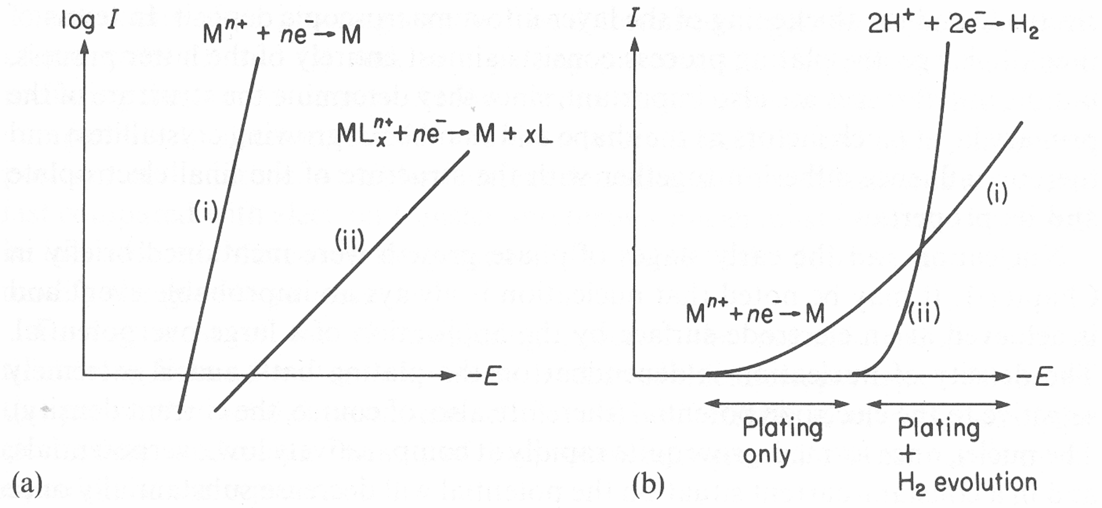


Fig. 8.4 (a) Tafel plots showing the common effects of the addition of a complexing agent to a plating bath on the reduction of the metal ion. (b) I–E plots for a metal ion and proton reduction in a plating bath.

금속 이온과 리간드의 강한 착물을 형성하거나 수소 발생의 경우 전류가 감소하여 느린 속도로 도금이 일어나 도금층의 질이 좋아짐

Pletcher, ch.8

Resistive substrates

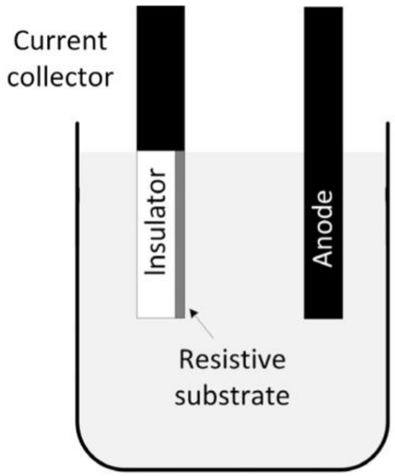


Figure 13.15 Schematic diagram of deposition cell for deposition on a resistive substrate where the potential drop in the substrate is important.

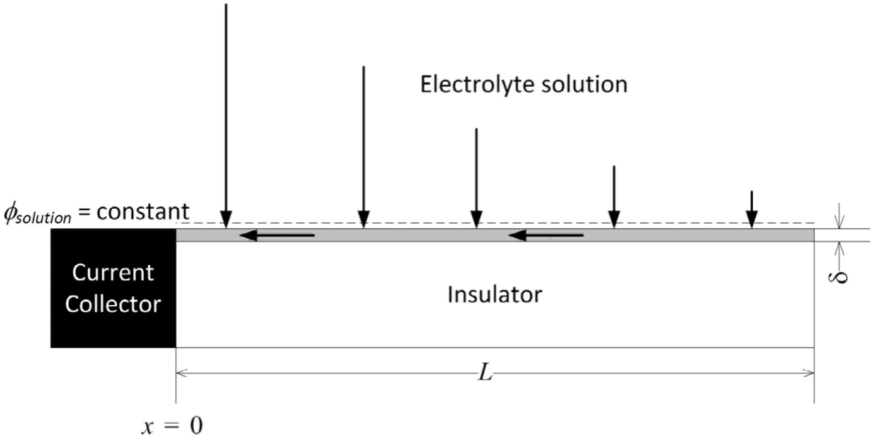


Figure 13.16 Schematic diagram of the physical situation described by the model below. ϕ_{metal} decreases from $x = L$ to $x = 0$ (not shown). Current flow shown qualitatively by filled arrows.

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

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

Typical application areas for electroplating

(1) Corrosion protection
(2) Build-up material or restoration
(3) Decorative appeal
(4) Wear resistance
(5) Hardness
(6) Optical or thermal reflectivity
(7) Electrical conductivity
(8) Ease of cleaning
(9) Oil retention
(10) Solderability
(11) Thermal conductivity

Advantages and drawbacks of electrodeposition as a coating technology

0.01 ~ 100 μm

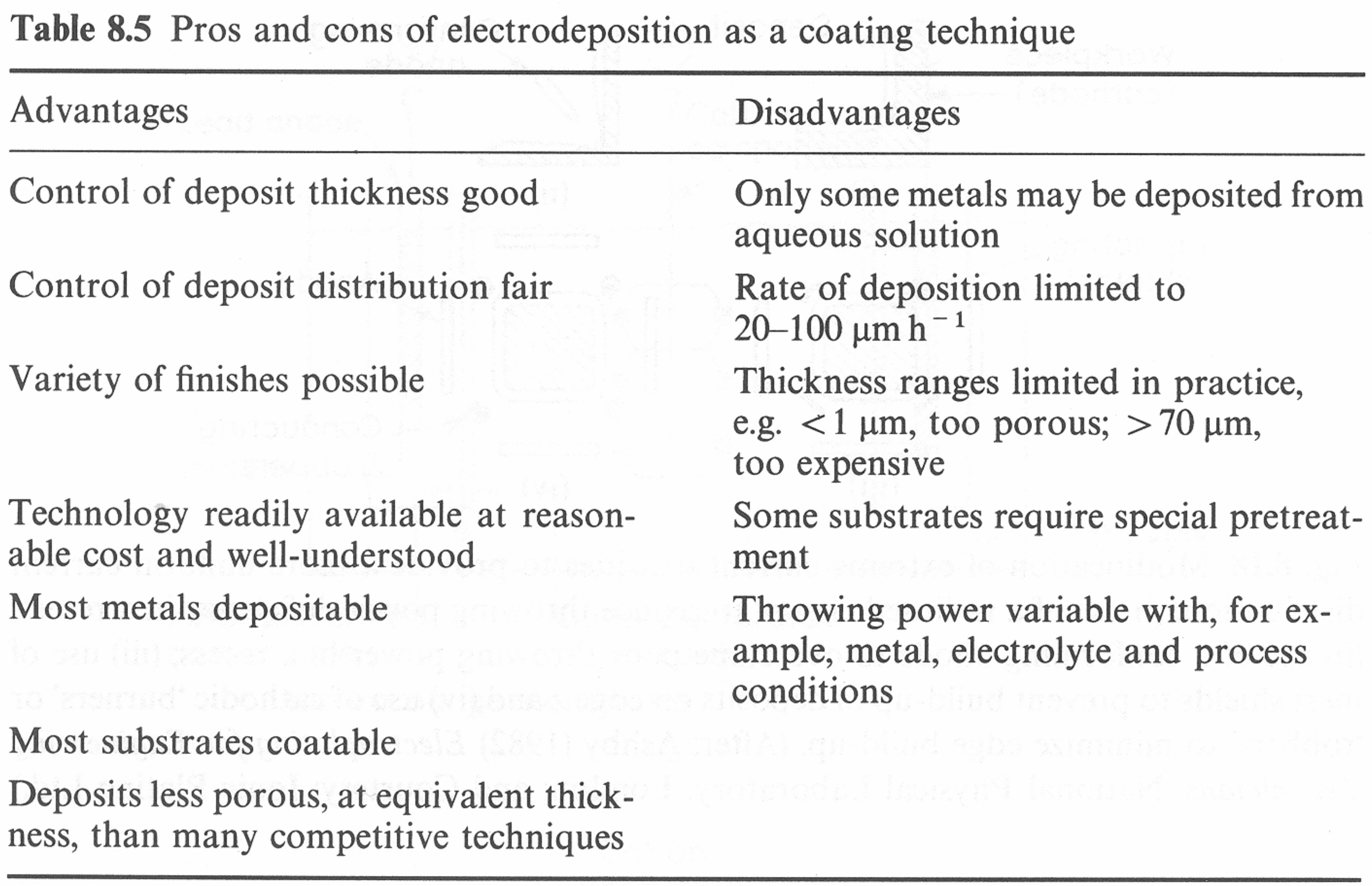


Table 8.5 Pros and cons of electrodeposition as a coating technique

Advantages	Disadvantages
Control of deposit thickness good	Only some metals may be deposited from aqueous solution
Control of deposit distribution fair	Rate of deposition limited to 20–100 $\mu m\ h^{-1}$
Variety of finishes possible	Thickness ranges limited in practice, e.g. $<1\ \mu m$, too porous; $>70\ \mu m$, too expensive
Technology readily available at reasonable cost and well-understood	Some substrates require special pretreatment
Most metals depositable	Throwing power variable with, for example, metal, electrolyte and process conditions
Most substrates coatable	
Deposits less porous, at equivalent thickness, than many competitive techniques	

Pletcher, ch.8

Alloy electrodeposition

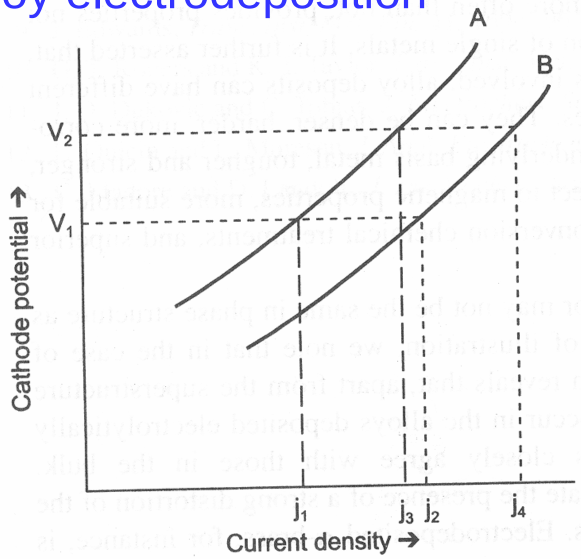


Figure 11.1. Polarization curves for the deposition of alloys. (From *Science and Technology of Surface Coating*—A NATO Advanced Study Institute publication, 1974, by permission of Academic Press.)

Paunovic. Schlesinger

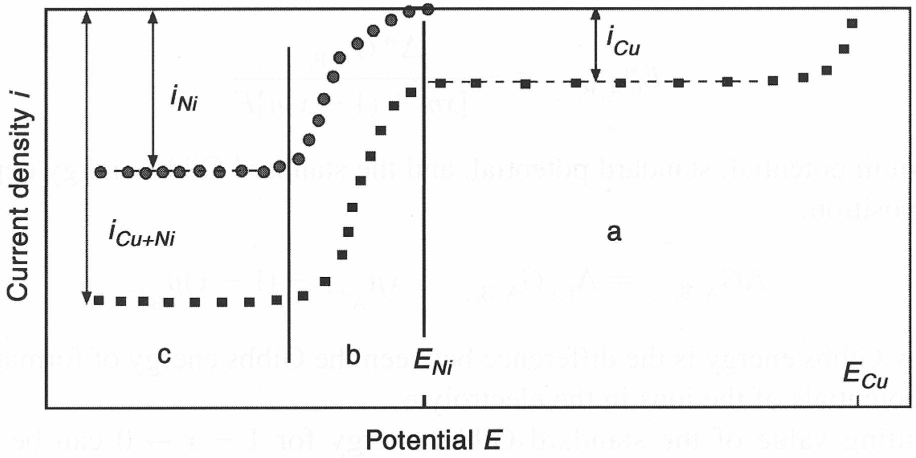
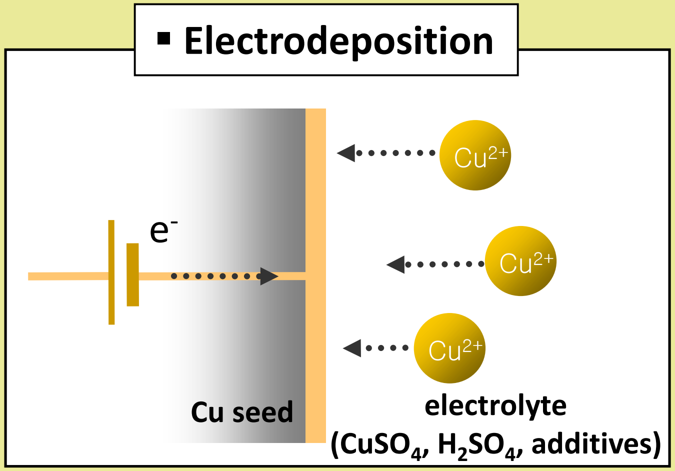


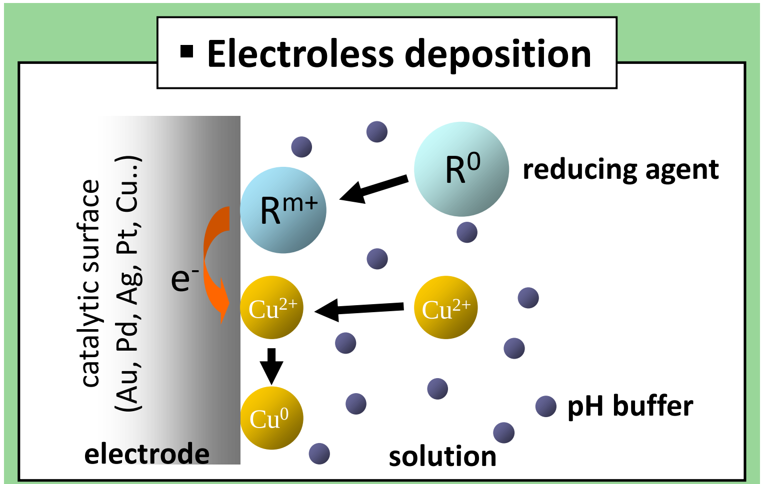
Figure 8.1 Voltammogram of CuNi alloy deposition with partial currents of Cu and Ni deposition and total deposition current; (a) copper deposition, (b) irregular co-deposition, (c) regular co-deposition. The names of the different alloy deposition regions refer to the classification of Brenner (see the following section).

Plieth

Electroless deposition (ELD): suitability for large area
Electrodeposition (ED): good film properties, high throwing power



(i) Cu reduction by an external power
(ii) High film quality, cheap process, high filling power
(iii) Electrode, seed layer, electrolyte
(iiii) Organic Additives



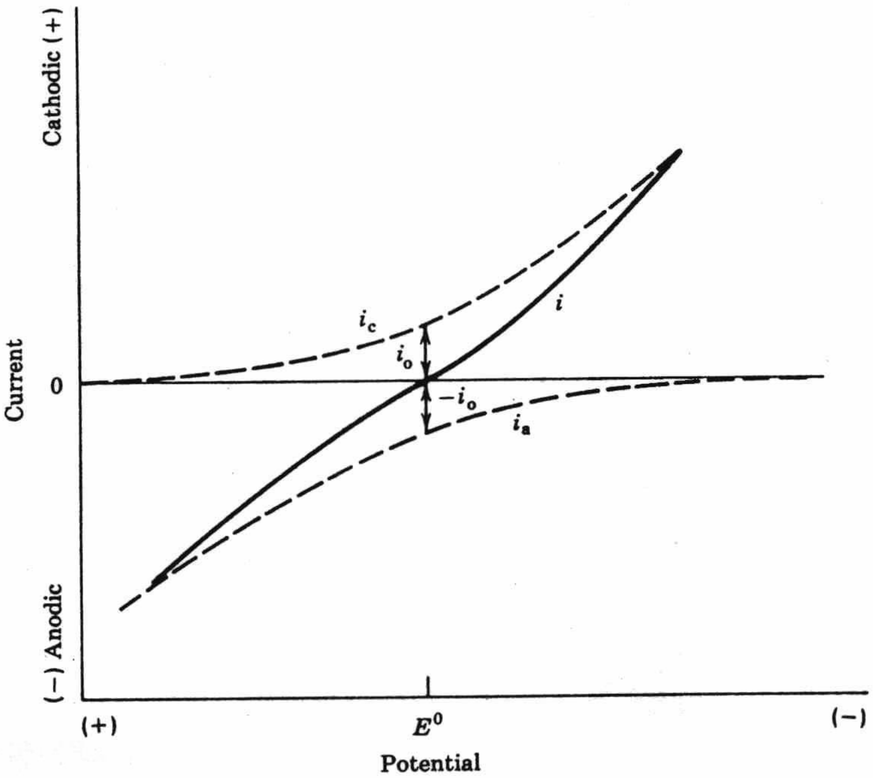
(i) Cu reduction by a reducing agent
(ii) Cheap process, feasibility on metal and insulator, highly conformal and uniform deposition
(iii) Electrolyte (reducing agent, additive)

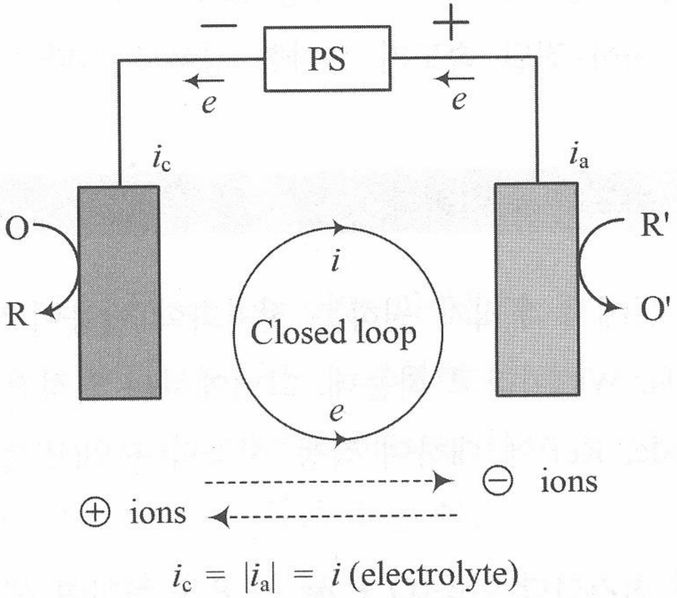
Plating possible on non-conductive materials such as glass and plastic (in some cases, a seed layer (<10 nm))

✓ **유리, 플라스틱 등 부도체에 도금 가능 (경우에 따라 씨앗층 형성(seed layer, <10 nm))**

From Prof. Oh-Joong Kwon (Incheon NU)

$O + ne^- = R$


Cathodic (+)
Current
0
(−) Anodic
i_c
i_o
$-i_o$
i_a
i
(+)
E^0
(−)
Potential


−
PS
+
e
e
i_c
i_a
O
R
R'
O'
i
Closed loop
e
⊖ ions
⊕ ions
$i_c = |i_a| = i$ (electrolyte)

I-V: Electroless deposition

Electrochemical Point of View: Mixed Potential Theory (혼성전위)

- Mixed potential theory: overlap of two independent electrochemical reaction

Metal ion reduction

$M^{n+} + ne^- \rightarrow M$

$$i_c = f(E)$$

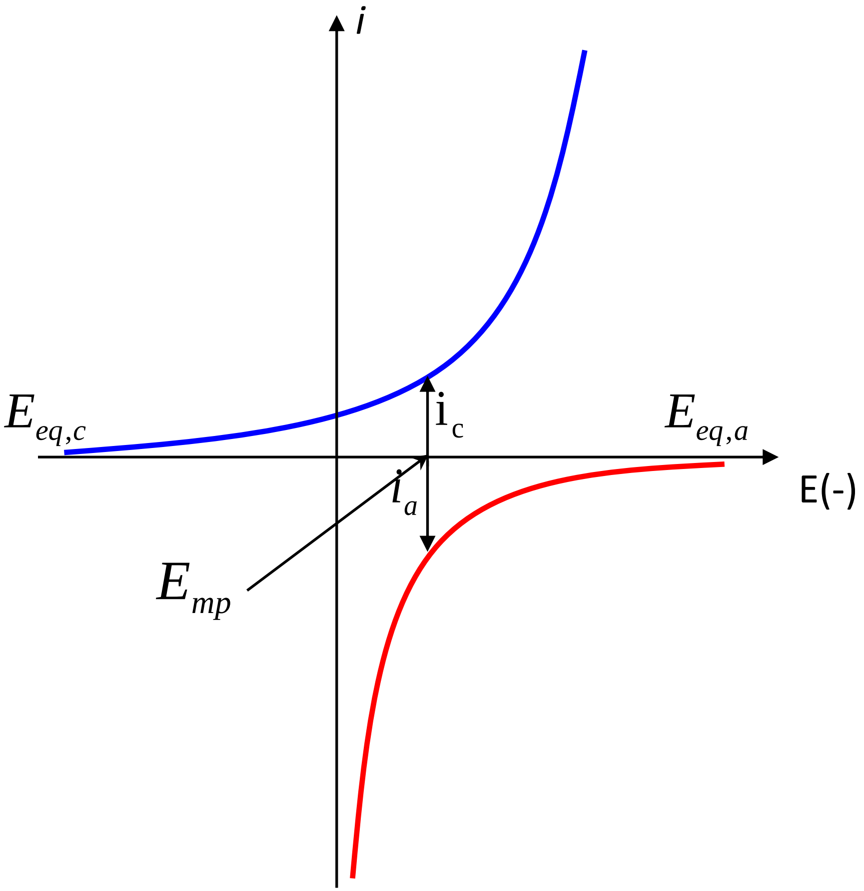
Reducing agent oxidation

$Red \rightarrow Ox^{m+} + me^-$

$$i_a = f(E)$$

- The potential where the total current becomes 0 is the mixed potential.

$$i_{total} = i_c + i_a$$



From Prof. Oh-Joong Kwon (Incheon NU)

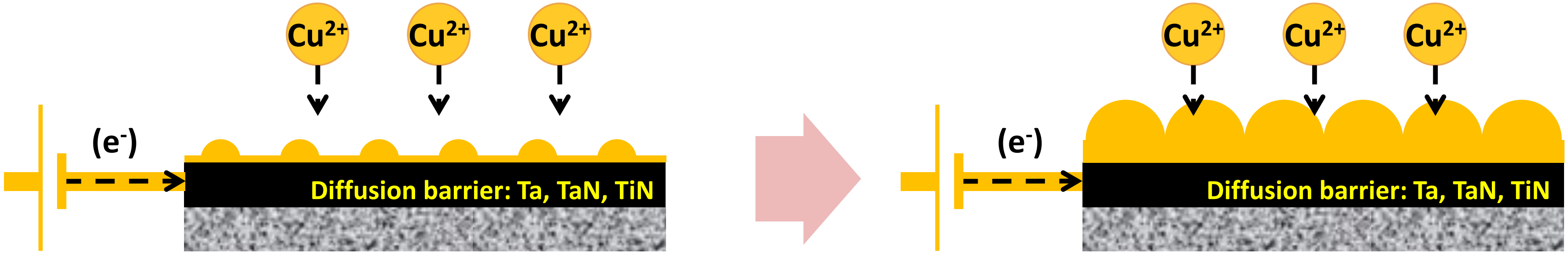
전기도금 (Electroplating)

✓ 금속(Cu, Ni, Au, Cr, Sn 등), 합금, 복합체(금속-Teflon 등)를 금속 표면에 전해공정을 통하여 전착(electrodeposition)시키는 것

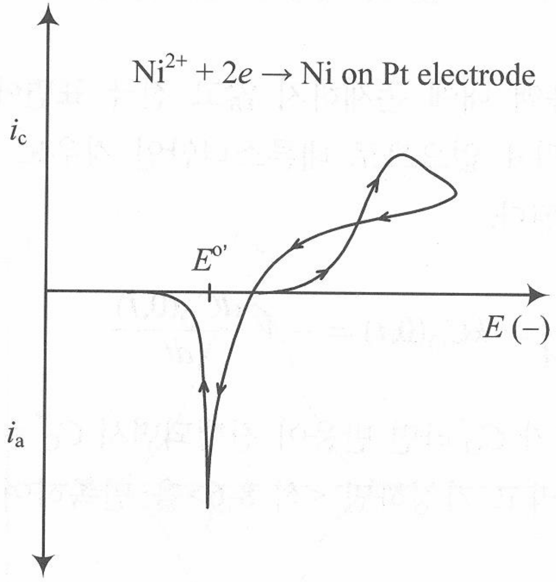
✓ 도금의 목적은 부식 방지, 전기 접촉 저항 조절, 장식, 마모성 억제 등 도금층의 질을 높이기 위해서는 도금 속도(전류)를 작게 유지 (전류가 크면 침상, 분말 상태로 도금, 혹은 강하게 결착되지 못함)

✓ 균일도를 높이기 위해 반응속도상수(k^0)가 작게 조절: 도금하고자 하는 금속 이온과 강하게 착물을 형성할 수 있는 리간드 첨가

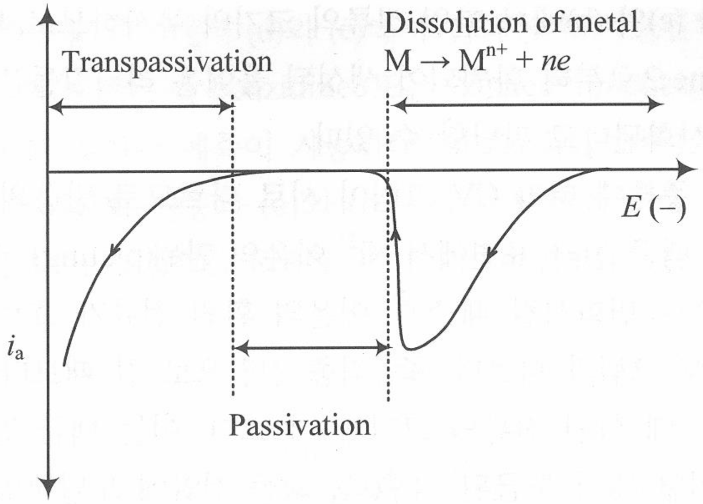
✓ 첨가제: 가속제(accelerator, 도금 속도를 증가), 억제제(inhibitor, 도금 속도를 감소), 광택제(brightener, 표면 균일, 광택) 등



Electrochemistry for electroplating



[그림 8-15] Pt 전극에 Ni^{2+}의 도금(plating)과 용출(dissolution) 과정을 보여 주는 CV 그림

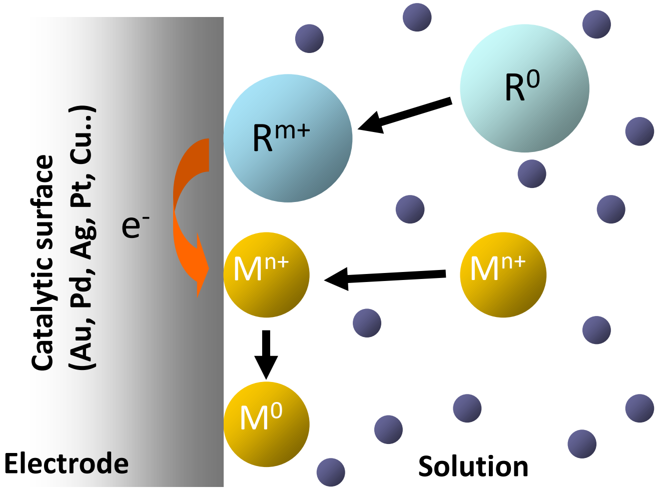


[그림 8-16] 금속(예; Cr)의 부동화 현상을 보여 주는 LSV 그림

Oh, ch.8

Electroless deposition

Definition of Electroless Deposition



- Chemical reduction process of metal ions in an aqueous solution without the use of electrical energy

● Metal ion

● pH buffer

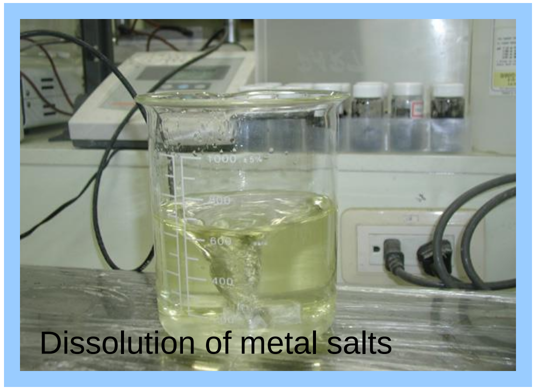
● Reducing agent

Reducing agents: Formaldehyde, hypophosphite, dimethylamine borane (DMAB), glyoxylic acid, Fe(II), Co(II), etc.
Complexing agents: EDTA, Mal, Suc, tartrate, TEA, En, etc.
Additives: Stabilizers (V, Mo, Ag, thiosulfate, sylfate, pyridines, 2-2’ dipyridyl, etc.), surfactants or wetting agents (anionic, non-ionic, amphoteric, cationic surfactants)

- Oxidation of reducing agent on surface
- Metal ion reduction on surface
- Continuous film growth
- Catalyzing of the oxidation of reducing agent on both substrate and metal film itself

From Prof. Oh-Joong Kwon (Incheon NU)

Procedure of Preparation for Pt-based Alloy Nanoparticles


Dissolution of metal salts


Reduction by $NaBH_4$


Washing & Filtering

Borohydride reduction method

$$PtCl_6^{2-} + BH_4^- + 3\,H_2O \rightarrow Pt + BO_3^{3-} + 6\,Cl^- + 6\,H^+ + 2\,H_2$$

$$4\,RuCl_3 + 3\,BH_4^- + 9\,H_2O \rightarrow 4\,Ru + 3\,BO_3^{3-} + 12\,Cl^- + 18\,H^+ + 6\,H_2$$

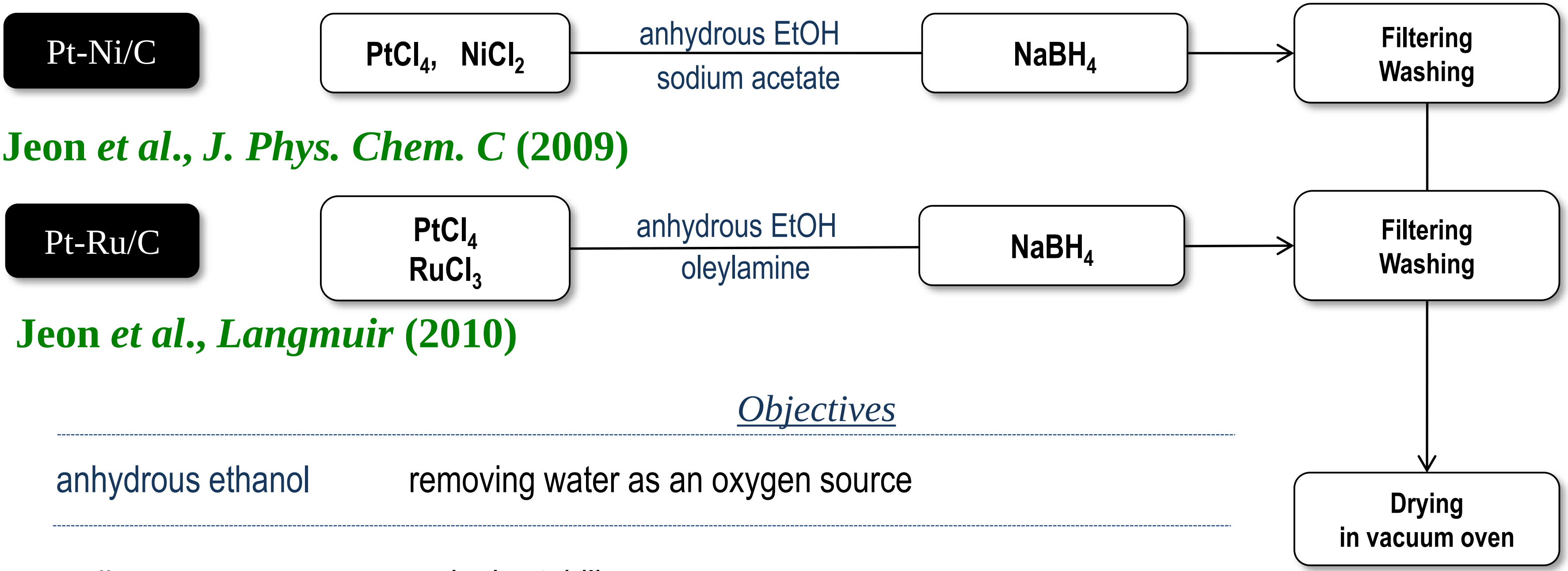

Freezing of precipitates


Freeze-Drying


Nanoparticles

Freeze-drying is a process in which samples are first frozen and then subjected to high vacuum (10^{-2} mbar). Under these conditions frozen water will sublime. Freeze drying preserves sediment structures in fast-frozen sediment (using liquid N_2). Sediments become very friable, making it easy to pick macrofossils or grind samples for chemical analyses.

Synthesis of PtNi alloy nanoparticle



Pt-Ni/C

$PtCl_4$, $NiCl_2$ → anhydrous EtOH, sodium acetate → $NaBH_4$ → Filtering Washing

Jeon *et al.*, *J. Phys. Chem. C* (2009)

Pt-Ru/C

$PtCl_4$, $RuCl_3$ → anhydrous EtOH, oleylamine → $NaBH_4$ → Filtering Washing

Jeon *et al.*, *Langmuir* (2010)

Filtering Washing → Drying in vacuum oven

Objectives

anhydrous ethanol	removing water as an oxygen source
sodium acetate	anionic stabilizer
oleylamine	stabilizer, to modify the surface charge of carbon black and enhance the heterogeneous nucleation of metal nanoparticles

Electroless deposition

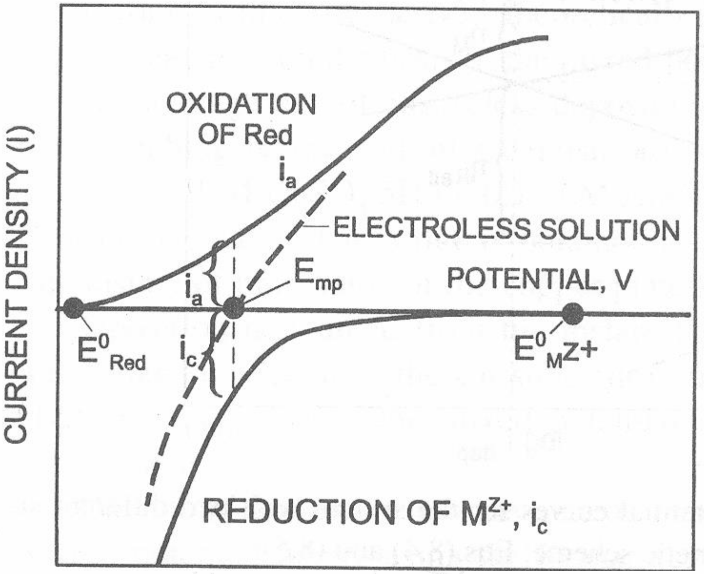


Figure 8.2. Wagner–Traud diagram for the total (i_{total} and component current potential curves (i_a, i_c) for the overall reaction of electroless deposition

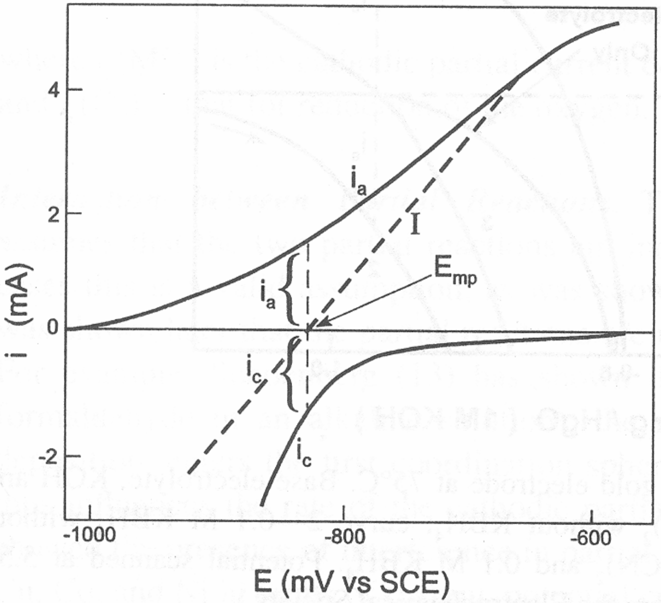


Figure 8.5. Wagner–Traud diagram for electroless Ni(B) deposition: $E_{mp} = -840$ mV versus SCE. Electrode area 0.68 cm^2. (From Ref. 43, with permission from the American Electroplaters and Surface Finishers Society.)

Pletcher, ch.8

Electroless deposition

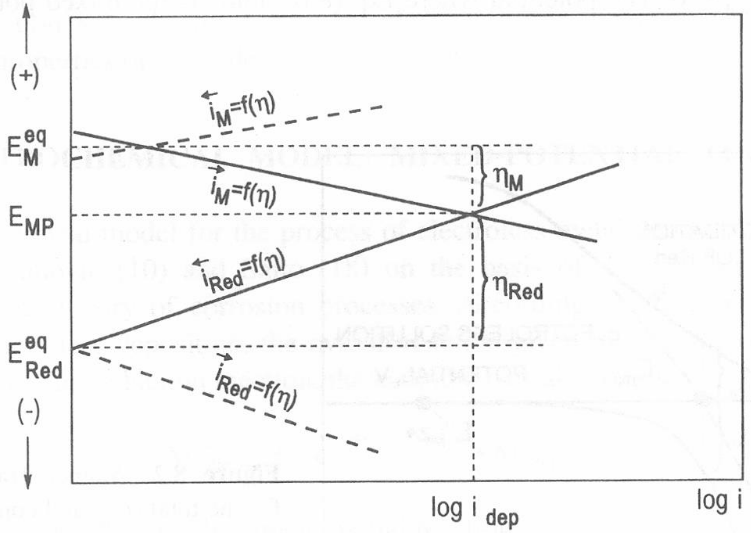


Figure 8.3. Evan diagram of current–potential curves for the system with two different simultaneous electrochemical reactions. Kinetic scheme: Eqs.(8.4) and (8.5).

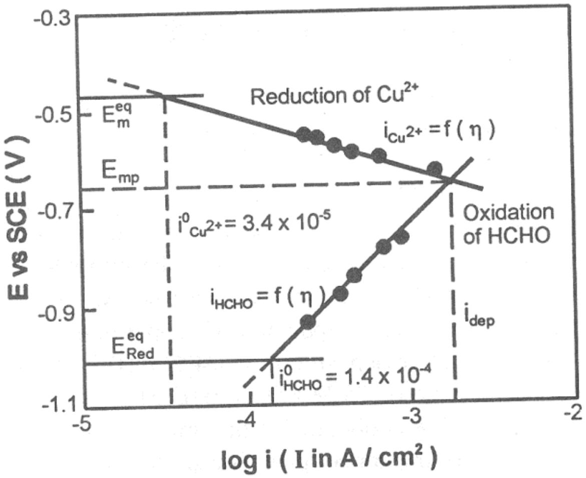


Figure 8.4. Current–potential curves for reduction of Cu^{2+} ions and for oxidation of reducing agent Red, formaldehyde, combined into one graph (Evans diagram). Solution for the Tafel line for the reduction of Cu^{2+} ions—0.1 M $CuSO_4$, 0.175 M EDTA, pH 12.50, $E_{eq}(Cu/Cu^{2+}) = -0.47$ V versus SCE; for the oxidation of formaldehyde—0.05 M HCHO and 0.075 M EDTA, pH 12.50, $E_{eq}(HCHO) = -1.0$ V versus SCE; temperature 25°C (±0.5°C). (From Ref. 10, with permission from the American Electroplaters and Surface Finishers Society.)

Pletcher, ch.8

Cu electroless deposition

Reducing agent:
formaldehyde(HCH=O)
EDTA-Cu complex
Pd seeded surface (catalyzed)

HCH=O adsorption on Pd

→ electrons evolving (HCH=O reduction, reducing agent)

→ Cu depostion

$Cu^{2+} + e^{-} \rightarrow Cu^{+}$ (rds, 율속단계)
$Cu^{+} + e \rightarrow Cu$ (fast)

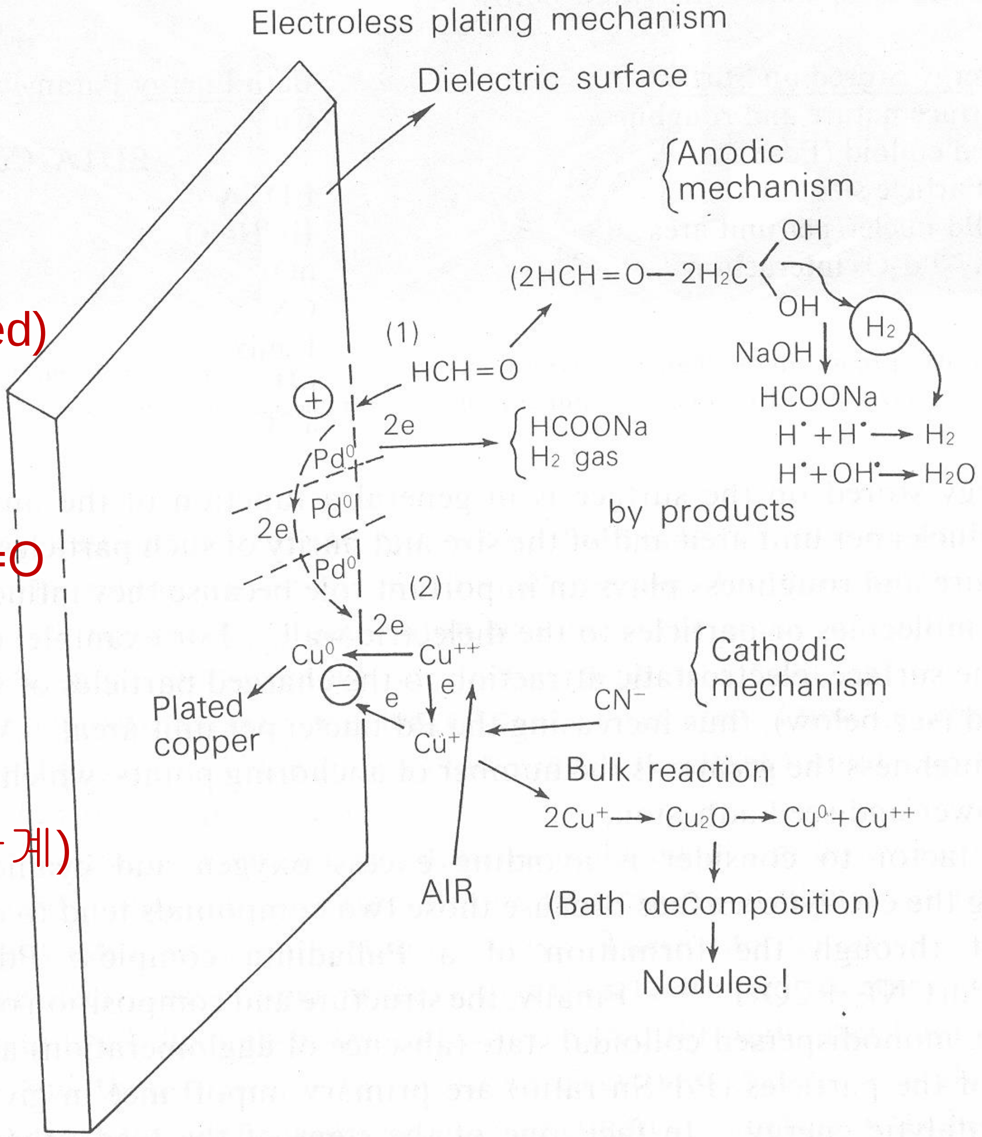


Fig. 5.2 Representation of the simultaneous partial reactions occurring on a Pd catalyzed surface at the initiation of the electroless deposition process, and the main reaction products.

Pletcher, ch.8

Conversion coating

- Electrochemical treatments to produce inorganic ‘conversion coatings’ on a metal: surface layers including oxides, chromates, phosphates and their mixtures
- Treatments under open circuit or by an impressed current

(1) Anodizing

- The process of forming a surface oxide film by electrochemical oxidation
- Surface-finishing technique for Al, Ti, Cu, steel, and for the manufacture of electrolytic capacitors based on Al, Ta, Nb(niobium)
- Al is anodized in an acid electrolyte, usually 10% sulfuric acid, chromic acid, sulfuric acid/oxalic acid mixtures.

  Anode: $2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$

  Cathode (inert cathode, steel or Cu): $6H^+ + 6e^- \rightarrow 3H_2$
- 2~100 μm for several minutes to 1 hour
- Color finishes: (i) an organic dye in adsorbed on the anodized surface and sealed with boiling water, (ii) a metal (Ni, Co, Sn) is deposited into the pores using an a.c. power supply; ‘electrocolouring’ process (interference effect, various colors, Sn(pale gold, bronze, black…)

(2) Phosphating

- Phosphate coatings provide an underlayer for paint finishes
- Substrate: steel, Zn, Al
- Advantages of phosphate coatings are improved corrosion resistance and paint adhesion
- Thin coating of mixed iron and zinc phosphate on steel as a standard pretreatment before painting of automotive bodies, refrigerators, washing machines (In case of car bodies, electrophoretic painting usually follows the phosphate coating)
- Phosphating bath: (i) phosphoric acid, (ii) a primary metal phosphate, (iii) an accelerator → dissolution of metal(Fe, Zn, Mn) and oxide, followed by the deposition of an insoluble phosphate layer
- Open circuit processing, but cathodic & (especially) anodic stimulation of the process for shorter process times & improved control of the deposited film

(3) Chromating

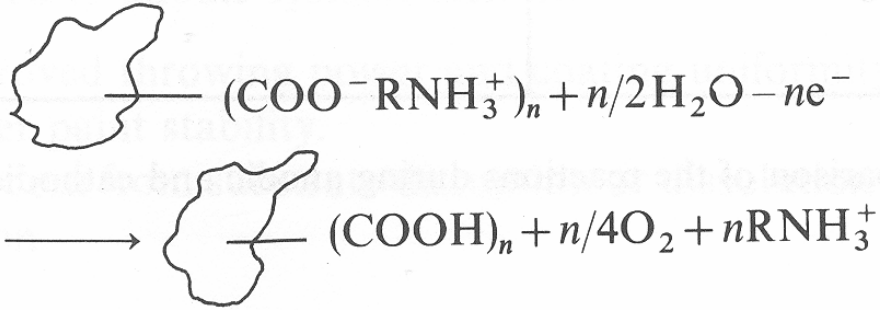
- Despite their toxicity, chromate solutions are widely used to provide protective and decorative coatings on Al and Mg-Al alloys, Zn, Cd

Electrophoretic coating

- When the substrate is conducting, electrophoretic deposition is carried out

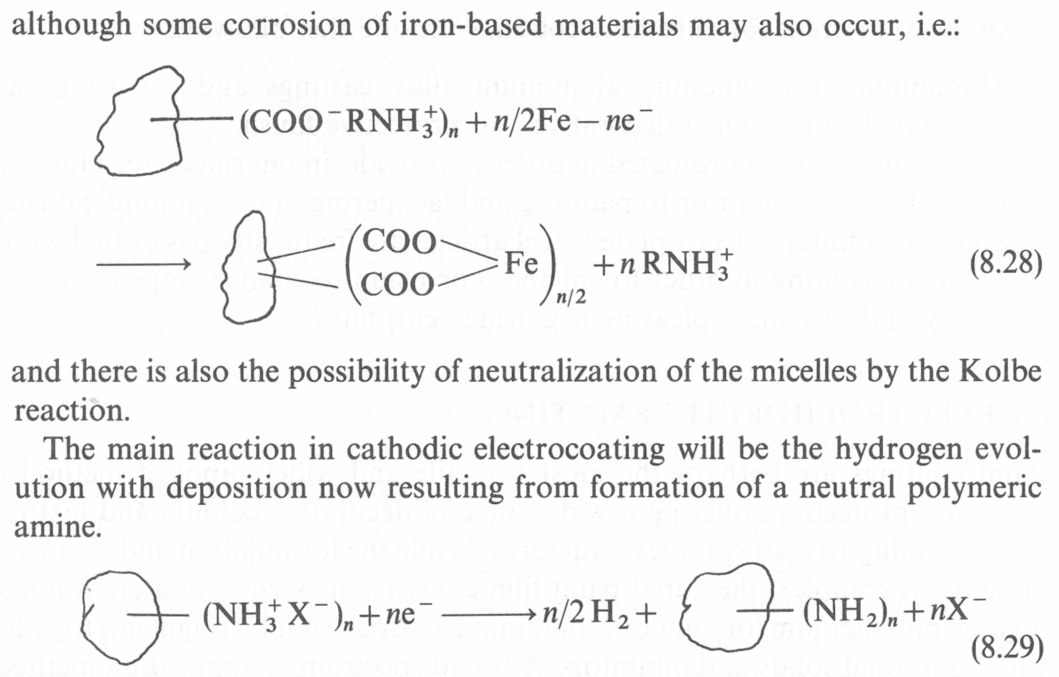
Principles of electrophoretic painting

- The medium for electrophoretic painting is water, sometimes containing a low percentage of an organic cosolvent
- The paint is a polymer containing: (i) acidic or basic groups which may be solubilized, usually to give micelles by the addition of base of acid respectively, (ii) some inorganic solids such as copper chromate, titanium dioxide or carbon black, (iii) an organic pigment to give the desired colour. The bath contains about 10% solids.
- When a voltage is applied between electrodes, deposition will occur at one of them, depending on the charge on the polymer, one will observe anodic or cathodic electrocoating (Fig. 8.23).
- Anodic process



$$(COO^{-}RNH_3^{+})_n + n/2H_2O - ne^{-} \longrightarrow (COOH)_n + n/4O_2 + nRNH_3^{+}$$

- Cathodic process



although some corrosion of iron-based materials may also occur, i.e.:

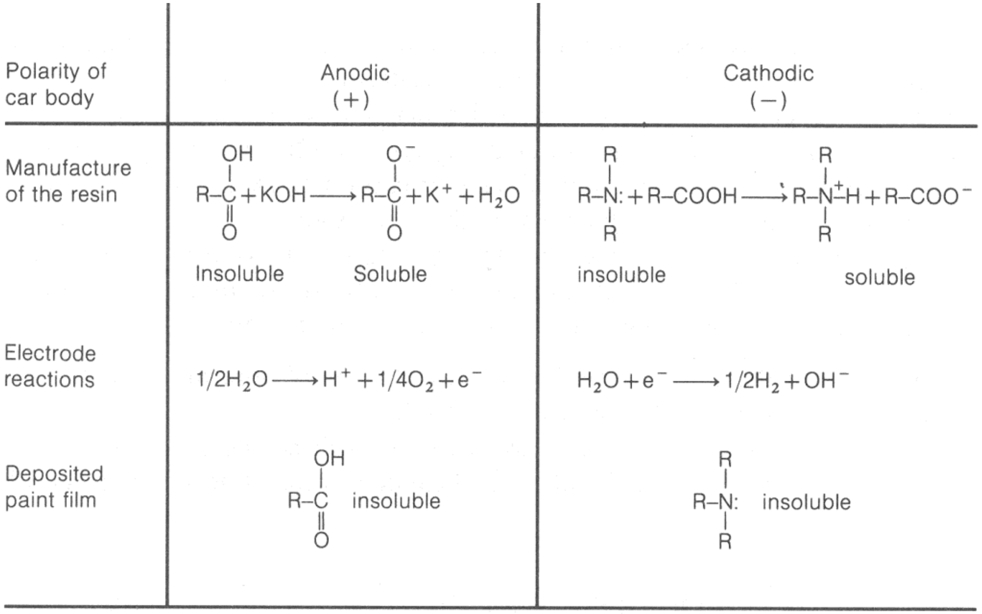
$$—(COO^-RNH_3^+)_n + n/2Fe - ne^-$$

$$\longrightarrow \left(\begin{matrix}COO \\ COO\end{matrix}\!>Fe\right)_{n/2} + n\,RNH_3^+ \qquad (8.28)$$

and there is also the possibility of neutralization of the micelles by the Kolbe reaction.

The main reaction in cathodic electrocoating will be the hydrogen evolution with deposition now resulting from formation of a neutral polymeric amine.

$$—(NH_3^+X^-)_n + ne^- \longrightarrow n/2\,H_2 + —(NH_2)_n + nX^- \qquad (8.29)$$



Polarity of car body	Anodic (+)	Cathodic (−)
Manufacture of the resin	$R\text{–}C(OH){=}O + KOH \longrightarrow R\text{–}C(O^-){=}O + K^+ + H_2O$ Insoluble Soluble	$R_3N: + R\text{–}COOH \longrightarrow R_3N^+\text{–}H + R\text{–}COO^-$ insoluble soluble
Electrode reactions	$1/2H_2O \longrightarrow H^+ + 1/4O_2 + e^-$	$H_2O + e^- \longrightarrow 1/2H_2 + OH^-$
Deposited paint film	$R\text{–}C(OH){=}O$ insoluble	$R_3N:$ insoluble

Fig. 8.23 A simplified comparison of the reactions during anodic and cathodic electrophoretic painting.

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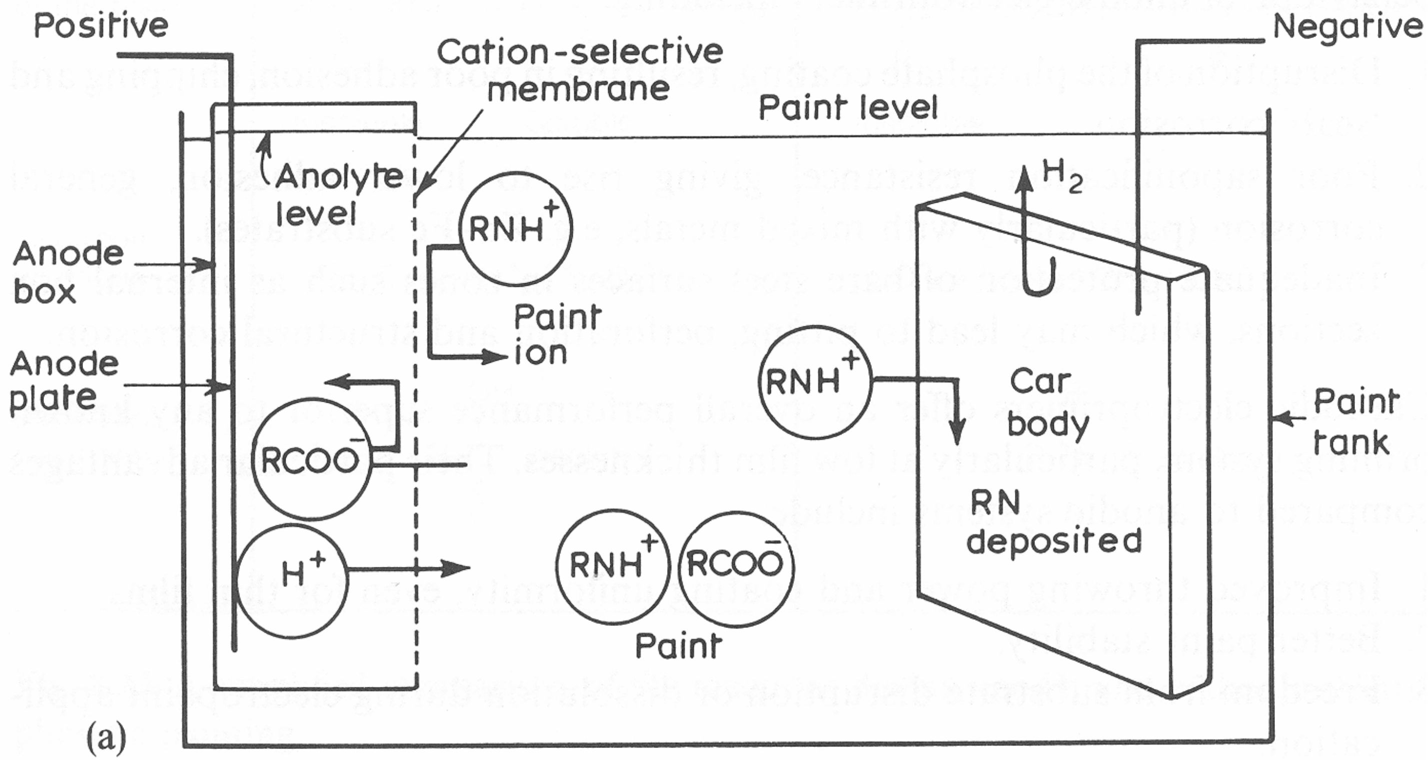

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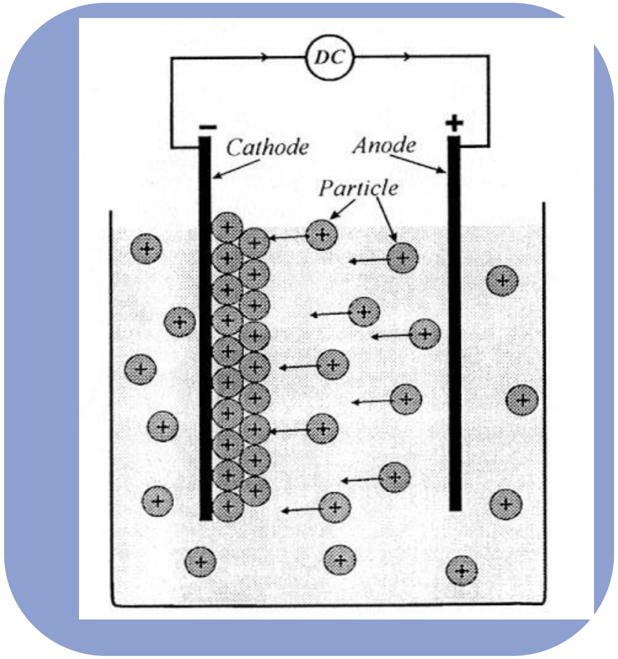
Electrophoretic Deposition

♠ Advantages

1. Fast and Low cost deposition
2. Short deposition time
3. Low contamination
4. Uniformity
5. Control packing density
6. Selectivity
7. Irregular deposition



♠ Applications

1. Ceramic (MgO, ZnO)
2. Super-conducting film (Bi-2223,BZT)
3. Phosphor
4. Electrode (fuel cell, Li battery)
5. Si carbide, Si nitride

• Mechanism

Electrophoresis

➡ Migration of charged particles in applied field Deposition

➡ Coagulation of particles to dense mass

♠ Electrophoretic Deposition

Solution: TiO_2 powder + $Mg(NO_3)_2 \cdot 6H_2O$ of 5 × 10^{-4} M in 80 ml IPA (~ 4.96 pH)
Applied Voltage: 150 V
Deposition time: 180 sec
Anode: SUS 304 (2 × 2 cm)
Cathode: Flexible ITO

Other electrochemical surface-finishing techniques

(1) Electropolishing

- A process used to produce metal articles with a highly reflective mirror finish; it is closely related to anodizing.

(2) Electrochemical cleaning

- To remove grease and oil from metal surfaces

(3) Electrochemical pickling

- To remove rust and other oxides and to produce a mild, uniform etch to enhance the adhesion of deposits

(4) Electrochemical stripping

- A deposit may be removed rapidly and selectively from the substrate by immersion in a suitable electrolyte

(5) Metalliding

- A deposition process carried out at elevated temperatures