Lecture Note #4 (Fall, 2020)

Transport

1. Nernst-Planck equation
2. I-V curve in mass transfer
3. Limiting current
4. Electrolyte transport
5. Overpotential or polarization

Fuller & Harb (textbook), ch.4, Bard (ref.), ch.1,4, Oh (ref.), ch.3,4

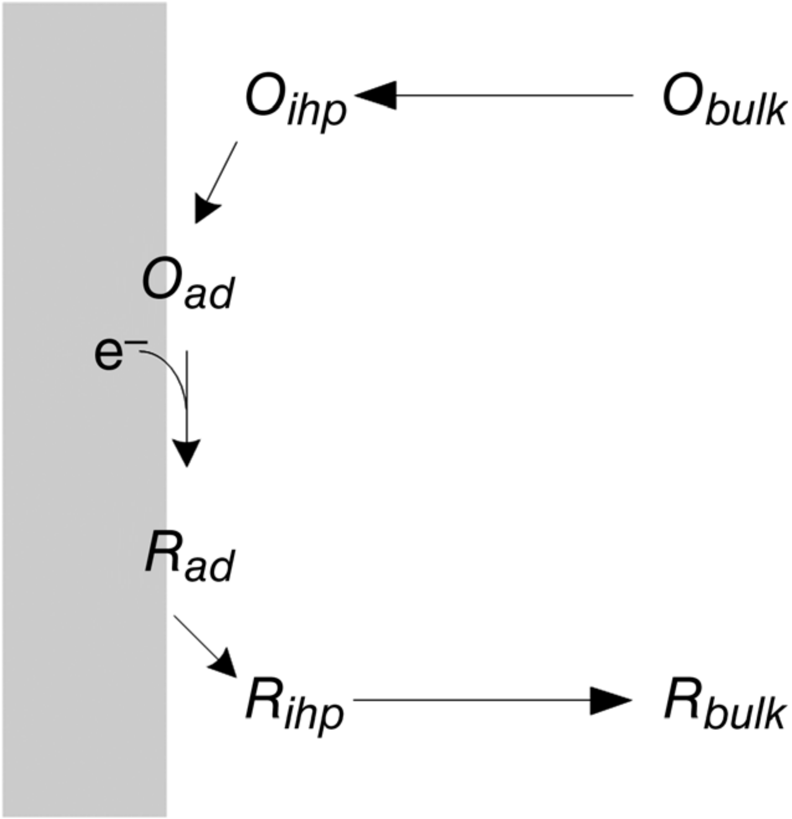

Figure 4.1 Multistep process for reduction.

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

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

Mass Transport

Mass transport

$$\text{rate} = k_a \mathbf{C_R^s} - k_c \mathbf{C_O^s}$$

Electrochemical reaction at electrode/solution interface: molecules in bulk solution must be transported to the electrode surface → "mass transfer"

$$C_O^b = C_O^s = C_R^s = C_R^b$$

Mechanisms for mass transport:

(a) Migration: movement of a charged body under the influence of an electric field (a gradient of electric potential)

(b) Diffusion: movement of species under the influence of gradient of chemical potential (i.e., a concentration gradient)

(c) Convection: stirring or hydrodynamic transport

Nernst-Planck equation (diffusion + migration + convection)

$$J_i(x) = -D_i(\partial C_i(x)/\partial x) - (z_iF/RT)D_iC_i(\partial \phi(x)/\partial x) + C_iv(x)$$

Where $J_i(x)$; the flux of species i ($\text{molsec}^{-1}\text{cm}^{-2}$) at distance x from the surface, D_i; the diffusion coefficient (cm^2/sec), $\partial C_i(x)/\partial x$; the concentration gradient at distance x, $\partial \phi(x)/\partial x$; the potential gradient, z_i and C_i; the charge and concentration of species i, v(x); the velocity (cm/sec)

1. Steady state mass transfer

steady state, $(\partial C/\partial t) = 0$; the rate of transport of electroactive species is equal to the rate of their reaction on the electrode surface

In the absence of migration,

$$R = O + ne^-$$

The rate of mass transfer,

$$v_{mt} \propto (\partial C_R(x)/\partial x)_{x=0} = (C_R^b - C_R^s)/\delta$$

where x is distance from the electrode surface & δ: diffusion layer

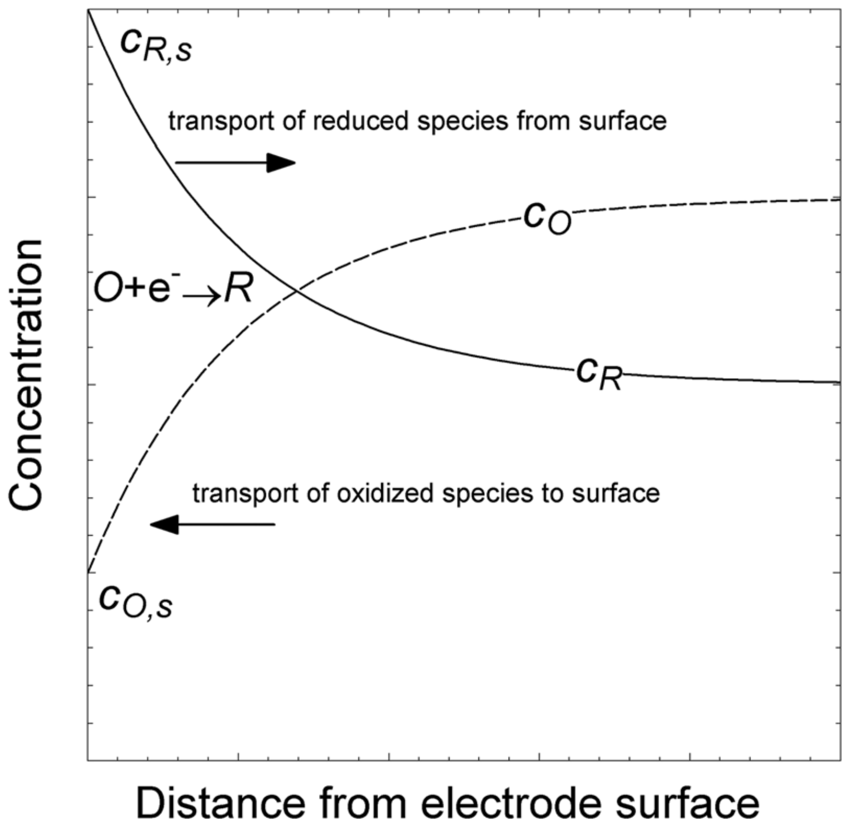

Figure 4.2 Concentration gradients associated with reduction of a solution-phase reactant at an electrode surface to form a soluble product.

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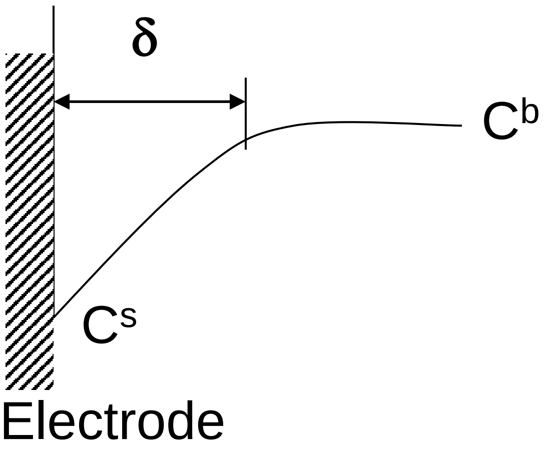


$$v_{mt} = m_R[C_R^b - C_R^s]$$

where C_R^b is the concentration of R in the bulk solution, C_R^s is the concentration at the electrode surface

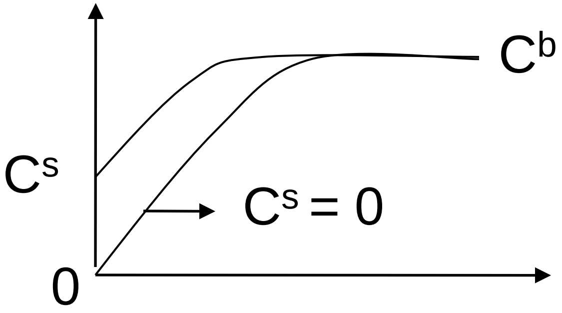
m_R is "mass transfer coefficient"

$$i = nFm_R[C_R^b - C_R^s]$$

$$i = -nFm_O[C_O^b - C_O^s]$$

largest rate of mass transfer of R when $C_R^s = 0$ → “limiting current”

$$\mathbf{i_{l,a} = nFm_R C_R^b}$$



$$C_R^s/C_R^b = 1 - (i/i_{l,a})$$

And

$$C_R^s = [1 - (i/i_{l,a})]\,[\,i_{l,a}/nFm_R] = (i_{l,a} - i)/(nFm_R)$$

Same method,

$$C_O^s/C_O^b = 1 - (i/i_{l,c})$$

$$i_{l,c} = nFm_O C_O^b$$

$$C_O^s = [1 - (i/i_{l,c})]\,[\,i_{l,c}/nFm_O] = (i_{l,c} - i)/(nFm_O)$$

Put these equations to $E = E^0 - (RT/nF)\ln(C_R^s/C_O^s)$

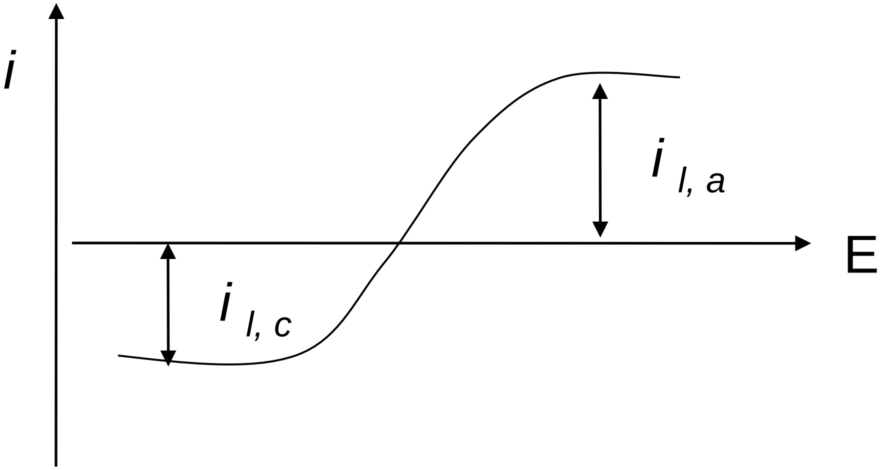
$$\mathbf{E = E^0 - (RT/nF)\ln(m_O/m_R) - (RT/nF)\ln[(i_{l,a} - i)/(i - i_{l,c})]}$$

Let

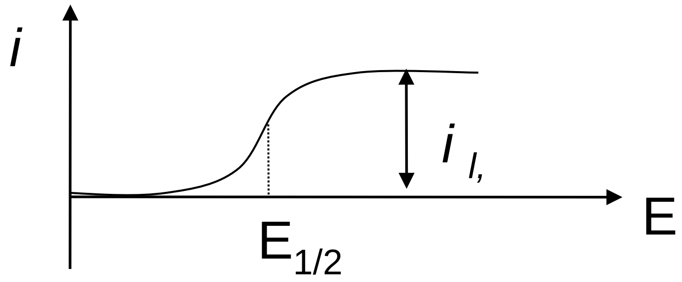
$$E_{1/2} = E^0 - (RT/nF)\ln(m_O/m_R)$$

Then,

$$E = E_{1/2} - (RT/nF)\ln[(i_{l,a} - i)/(i - i_{l,c})]$$



$E_{1/2}$, half-wave potential, independent of C_O^b and C_R^b → characteristic of the R/O system.



Reversibility:
<u>reversible</u>: $k^0 >> m_O$ or m_R → kinetic rate constant >> mass transport rate constant → system is at equilibrium at the electrode surface and it is possible to apply the Nernst equation at any potential

<u>irreversible</u>: $k^0 << m_O$ or m_R

2. Non-steady state mass transport: diffusion control

The rate of diffusion depends on the concentration gradients

$$J = -D(\partial C/\partial x) \quad \text{Fick's first law}$$

D: diffusion coefficient (cm^2/sec)

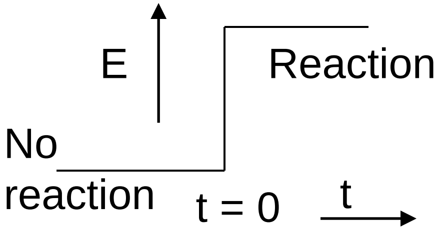
The variation of concentration with time due to diffusion → Fick's second law

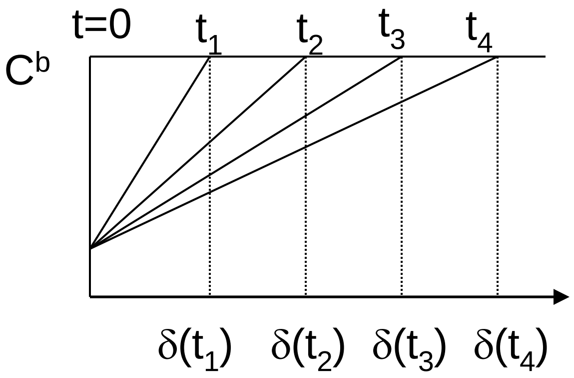
$$\partial C/\partial t = -D(\partial^2 C/\partial x^2) \qquad \text{1-D}$$

$$J = -D(\partial C/\partial x) = i/nF$$

$$D(\partial C/\partial x) = D(C^b - C^s)/\delta = i/nF$$

Time-dependent, applying potential step E





Moles of species in diffusion layer = $\int i dt/nF \approx [C^b - C^s](A\delta(t)/2)$

Differentiating,

$i/nF = [C^b - C^s](A d\delta(t)/2dt) = D(C^b - C^s)/\delta(t)$

$d\delta(t)/dt = 2D/\delta(t)$, $\delta(t) = 0$ at $t = 0$

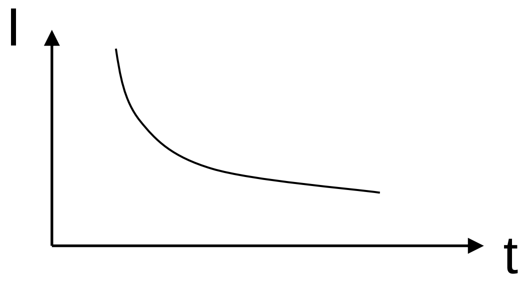
$\delta(t) = 2\sqrt{(Dt)}$

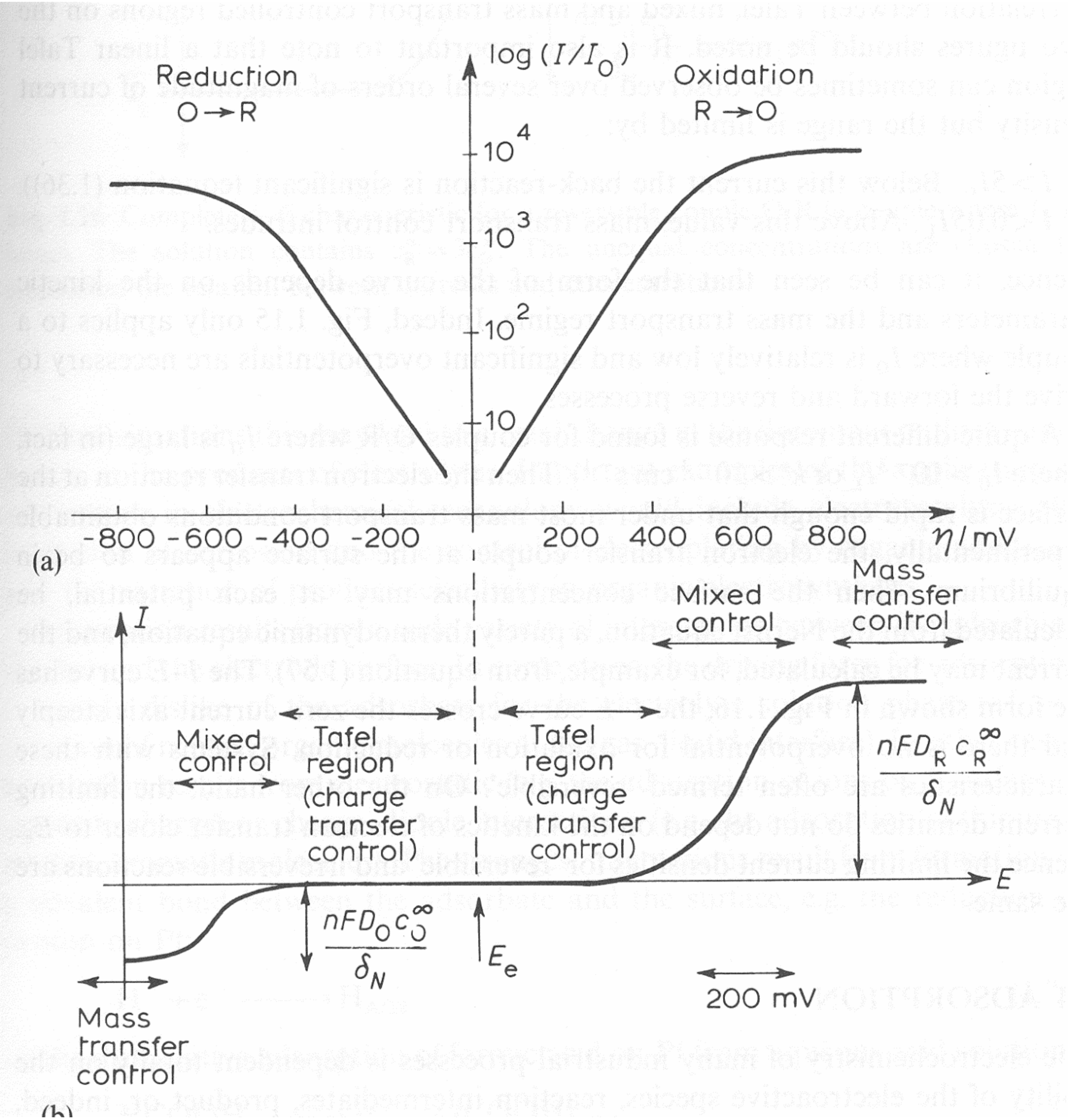
$$i/nF = (D^{1/2}/2t^{1/2})\ [C^b - C^s]$$

diffusion layer grows with $t^{1/2}$ and current decays with $t^{-1/2}$

potential step (chronoamperometry), planar electrode: Cottrell equation (in Lecture #6)

constant current → potential variation at time (chronopotentiometry): Sand equation (t = τ (transition time) at $C^s = 0$)





Pletcher, Fig. 1.8

Electrolyte

Mobility and transport number

Mobilities: conduction from the standpoint of the charge carriers

Electric current = rate at which charge crosses any plane = [number of carriers per unit volume][cross sectional area][charge on each carrier][average carrier speed]

$$I = dq/dt = (N_A c_i)(A)(q_i)(\nu_i)$$

i: particular charge carrier, c_i; concentration, q_i; charge, ν_i; average velocity,

N_A; Avogadro's constant (6.0220 x 10^{23} mol^{-1}), A; area

z_i; charge number = q_i/q_e where q_e (1.6022 x 10^{-19} C),

e.g., electrons:-1, Mg^{2+}; +2

$$\nu_i \propto f_i \propto X \propto d\phi/dx$$

f_i; force exerted on the charge carrier, X; electric field strength

mobility of the carrier, u_i ($m^2s^{-1}V^{-1}$ unit) = velocity to field ratio (ν_i / X)

$$\nu_i = \pm u_i X \ = -(z_i/|z_i|)u_i d\phi/dx$$

$|z_i|$: absolute value of the charge number

u_{e-} of electrons: 6.7 x 10^{-3} $m^2s^{-1}V^{-1}$ for Ag, less mobile in other metals
mobility of ions in aqueous solution: smaller than the factor of 10^5 (factor 10^5 slower); $u_{cu2+}{}^o$ = 5.9 x 10^{-8} $m^2s^{-1}V^{-1}$ in extremely diluted solution

Current I,

$$I = -A\,N_A q_e |z_i| u_i c_i d\phi/dx$$

If there are several kind of charge carriers,

$$I = -AFd\phi/dx\Sigma|z_i|u_i c_i$$

$$i = -Fd\phi/dx\Sigma|z_i|u_i c_i$$

Transport number t_i; the fraction of the total current carried by one particular charge carrier

$$t_i = (|z_i|u_ic_i)/\Sigma(|z_i|u_ic_i)$$

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

conductivity κ

$$\kappa = F\Sigma|z_i|u_ic_i$$

molar ionic conductivity (λ_i); Fu_i

Ion mobilities at extreme dilution in aqueous solution at 298 K

Ion	$u^o/m^2s^{-1}V^{-1}$
H^+	362.5×10^{-9}
K^+	76.2×10^{-9}
Ag^+	64.2×10^{-9}
Cu^{2+}	58.6×10^{-9}
Na^+	51.9×10^{-9}
Li^+	40.1×10^{-9}
OH^-	204.8×10^{-9}
SO_4^{2-}	82.7×10^{-9}
Cl^-	79.1×10^{-9}
ClO_4^-	69.8×10^{-9}
$C_6H_5COO^-$	33.5×10^{-9}

cf. u_{e-} of electrons: 6.7×10^{-3} $m^2s^{-1}V^{-1}$ for Ag

Conductivity

Electricity flows either by electron motion or ion motion
In both cases,
the intensity of the flow (= current density) $\propto$ electric field strength

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

conductivity κ

$$\kappa = F\Sigma |z_i| u_i c_i$$

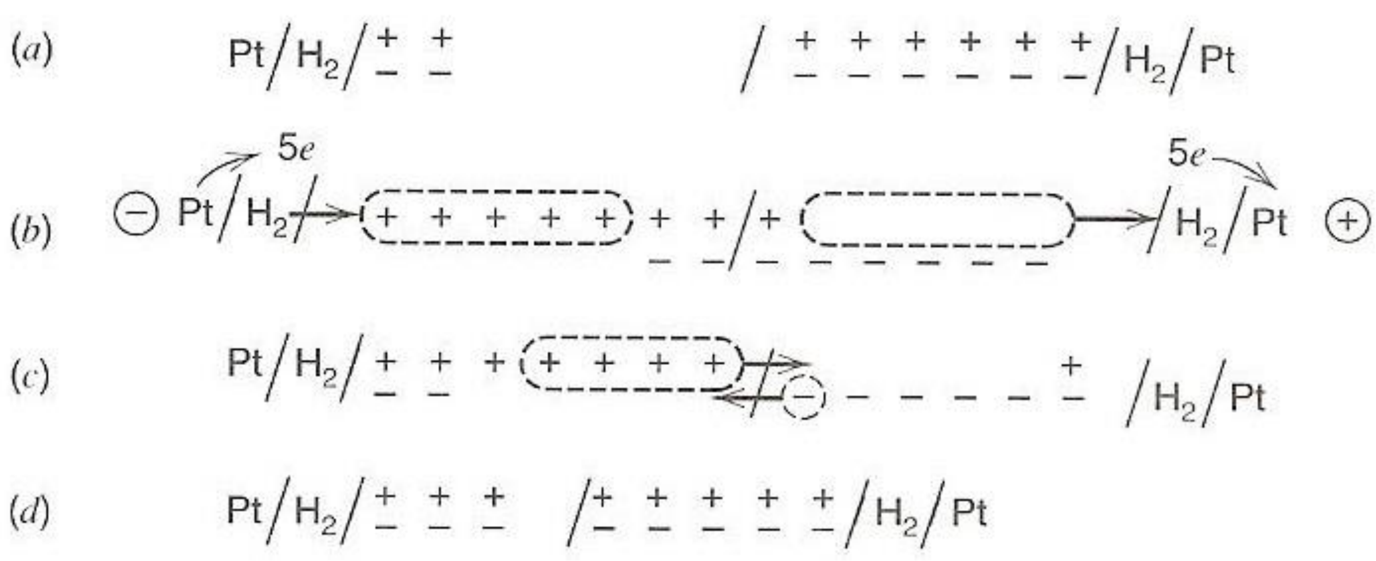
determined by the concentration of charge carriers and their mobilities

one form of Ohm's law

$$\Delta E = -RI$$

potential difference across resistor to the current flowing through it

Resistor: dissipate energy
Capacitor: store energy



Transference number (or transport number)

The fraction of the current carried by H^+ and Cl^-: t_+ and t_-

$$t_+ + t_- = 1$$

$$\sum t_i = 1$$

e.g., Figure above: $t_+ = 0.8$, $t_- = 0.2$

Conductance ($S = \Omega^{-1}$), $L = \kappa A / l$

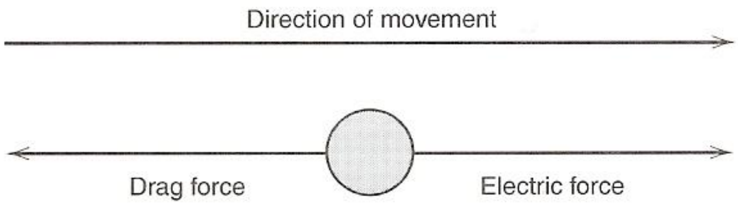
conductivity (κ, $S \cdot cm^{-1}$): contribution from all ionic species

$\propto$ ion conc, charge magnitude ($|z_i|$), index of migration velocity (u_i)

Mobility (u_i): limiting velocity of the ion in an electric field of unit strength

unit: $cm^2V^{-1}s^{-1}$ (cm/s per V/cm)

electric field, E → electric force → counterbalance with frictional drag → terminal velocity



Electric force = $|z_i|eE$ e: electronic charge

Frictional drag (Stokes law) = $6\pi\eta rv$

η :viscosity of medium, r: ion radius, v: velocity

When the terminal velocity is reached:

$$u_i = v/E = |z_i|e/ 6\pi\eta r$$

Conductivity

$$\kappa = F\sum|z_i|u_iC_i$$

Transference number for species i = conductivity by i /total conductivity

$$t_i = |z_i|u_iC_i/\sum|z_j|u_jC_j$$

For pure electrolytes(e.g., KCl, $CaCl_2$, HNO_3) → equivalent conductivity (Λ)

$$\Lambda = \kappa/C_{eq} \quad \text{(conductivity per unit concentration of charge)}$$

C_{eq}: concentration of + (or -) charges = C|z|

$$\Lambda = F(u_+ + u_-) = \lambda_+ + \lambda_-$$

equivalent ion conductivity, $\lambda_i = Fu_i$

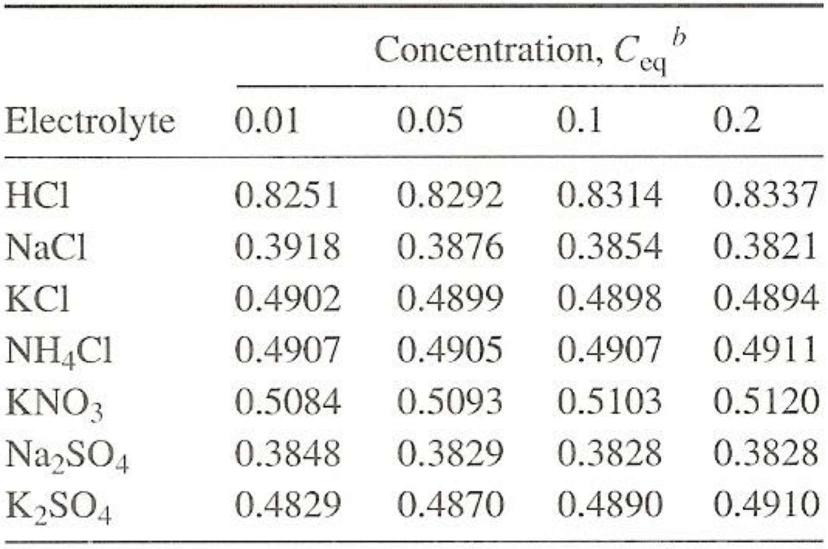
$$t_i = \lambda_i/\Lambda = u_i/(u_+ + u_-)$$

- Table: t_+ → individual ionic conductivities, λ_i
- λ_i, t_i depend on concentration of pure electrolyte because interactions between ions tend to alter mobilities

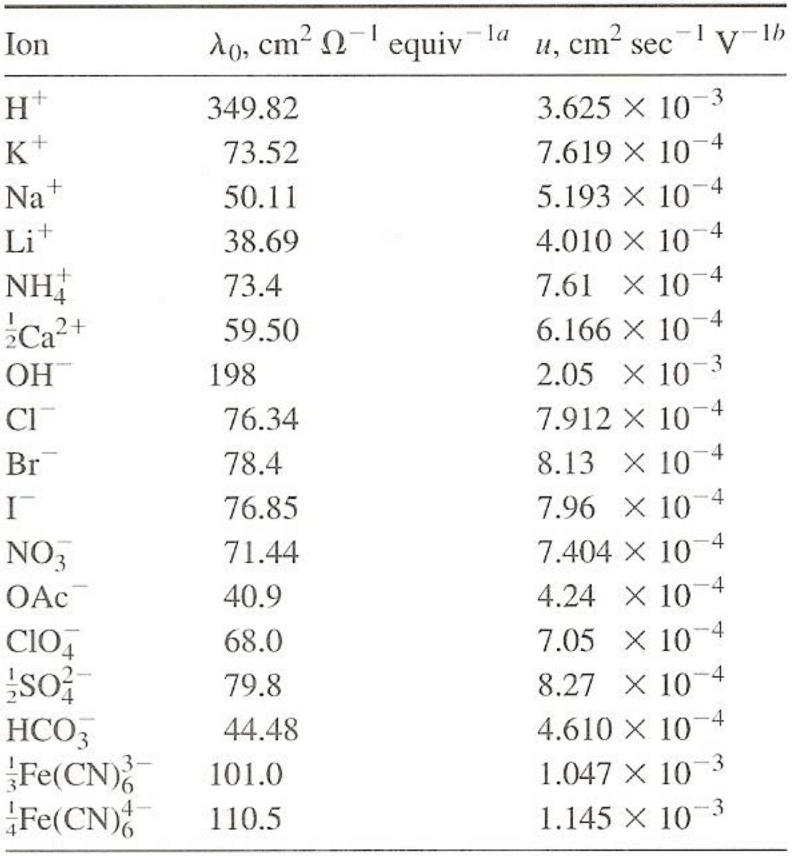
→ Table : λ_{0i} (extrapolated to infinite dilution) → calculate t_i

For pure electrolyte: $t_i = \lambda_i/\Lambda$

For mixed electrolytes: $t_i = |z_i|C_i\lambda_i/\sum|z_j|C_j\lambda_j$



	Concentration, C_{eq} [b]			
Electrolyte	0.01	0.05	0.1	0.2
HCl	0.8251	0.8292	0.8314	0.8337
NaCl	0.3918	0.3876	0.3854	0.3821
KCl	0.4902	0.4899	0.4898	0.4894
NH_4Cl	0.4907	0.4905	0.4907	0.4911
KNO_3	0.5084	0.5093	0.5103	0.5120
Na_2SO_4	0.3848	0.3829	0.3828	0.3828
K_2SO_4	0.4829	0.4870	0.4890	0.4910



Ion	λ_0, $cm^2\ \Omega^{-1}\ equiv^{-1}$ [a]	u, $cm^2\ sec^{-1}\ V^{-1}$ [b]
H^+	349.82	3.625×10^{-3}
K^+	73.52	7.619×10^{-4}
Na^+	50.11	5.193×10^{-4}
Li^+	38.69	4.010×10^{-4}
NH_4^+	73.4	7.61×10^{-4}
$\frac{1}{2}Ca^{2+}$	59.50	6.166×10^{-4}
OH^-	198	2.05×10^{-3}
Cl^-	76.34	7.912×10^{-4}
Br^-	78.4	8.13×10^{-4}
I^-	76.85	7.96×10^{-4}
NO_3^-	71.44	7.404×10^{-4}
OAc^-	40.9	4.24×10^{-4}
ClO_4^-	68.0	7.05×10^{-4}
$\frac{1}{2}SO_4^{2-}$	79.8	8.27×10^{-4}
HCO_3^-	44.48	4.610×10^{-4}
$\frac{1}{3}Fe(CN)_6^{3-}$	101.0	1.047×10^{-3}
$\frac{1}{4}Fe(CN)_6^{4-}$	110.5	1.145×10^{-3}

Solid electrolyte: ions move under electric field without solvent → conductivity → batteries, fuel cells, and electrochemical devices

Classes of conductors

Materials 1.Conductors Electronic conductors
Ionic conductors
2. Insulators

Conductors: metals
Insulators: plastics, ceramics, gases
No clear cut distinction between conductor and insulator

Typical value of electrical conductivity

	Material	$\kappa/\mathrm{Sm^{-1}}$
Ionic conductors	Ionic crystals	$10^{-16} – 10^{-2}$
	Solid electrolytes	$10^{-1} – 10^{3}$
	Strong(liquid) electrolytes	$10^{-1} – 10^{3}$
Electronic conductors	Metals	$10^{3} – 10^{7}$
	Semiconductors	$10^{-3} – 10^{4}$
	Insulators	$<10^{-10}$

S/m → x10^{-2} for S/cm

Electrical conductivity of various materials (most at 298 K)

Material	κ/Sm^{-1}	Charge carriers
Superconductors (low temp)	∞	Electron pairs
Ag	6.3×10^{7}	Electrons
Cu	6.0×10^{7}	Electrons
Hg	1.0×10^{6}	Electrons
C (graphite)	4×10^{4}	Pi electrons
Doped polypyrrole	6×10^{3}	Pi electrons
Molten KCl (at 1043 K)	217	K^+ and Cl^-
5.2 M H_2SO_4 (battery acid)	82	H^+ and HSO_4^-
Seawater	5.2	Cations & anions
Ge	2.2	Electrons and holes
0.1 M KCl	1.3	K^+ and Cl^-
H2O	5.7×10^{-6}	H^+ and OH^-
Typical glass	3×10^{-10}	Univalent cations
Teflon, $(CF_2)n$	10^{-15}	?
Vacuum & most gases	0	

Measurement of electrical conductivity

1. Four terminal method: κ calculation from measured I, $\Delta\phi$, A and x

2. a.c. impedance method

The nature of the charge carriers

1) Electronic conductors: mobile electrons; metals, some inorganic oxides and sulfides (e.g., PbO_2 and Ag_2S which are slightly non-stoichiometric), semiconductors (n-type: electrons, p-type: holes, intrinsic: both), conducting polymer (pi-electrons), graphite(pi-electrons), organic metals (organic salts, e.g., TTF-TCNQ(tetrathiafulvalene tetracyanoquinodimethane, pi-electrons)

- Metals: shared valence electrons with all atoms in solid (delocalized electrons) → high electric and thermal conductivity

cf: insulator vs. conductor: valence band completely filled vs. partially filled e.g., Diamond (insulator); sp^3 orbital (completely filled valence band), E_g: 5.6 eV

Na (alkali metal); 11 electrons (10 filled 1s & 2p, 1 valence electron 3s (half filled → electric conduction using unfilled part of VB)

Alkaline earth metal (divalent, 12 e's) → good conductors because their valence band overlaps another band

Conductivity of metal increases as temperature lowered or impurities reduced since low resistance

- Semiconductors: E_g is smaller than insulator (1 ~ 2 eV; relatively small excitation energy, cf) 1eV = 12000 K = 1240 nm (1.2 μm (IR))

Conductivity of semiconductors increases as temperature & impurity concentration increased.

- Semimetals; between metals & semiconductors, e.g., graphite → planar sheet of hexagons with weak van der Waals forces (2-dimensional molecule), $E_g = 0$ (top energy level of pi(π)-bonding orbitals (the valence band) is at the same level of that of the anti-bonding orbital

- Conducting polymer: π-electrons

2) Ionic conductors: motion of anions and/or cations; solutions of electrolytes (salts, acids and bases) in water and other liquids, molten salts, solid ionic conductors (solid electrolyte)(O^{2-} in ZrO_2 at high temperature, Ag^+ in $RbAg_4I_5$ at room temperature, fluoride ion holes in EuF_2 doped LaF_3)

3) <u>Electronic & ionic conductors</u>; plasmas (hot gases, positive ions and free electrons), sodium metal in liquid ammonia(Na^+ cation and solvated electrons), hydrogen dissolved in Pd metal(hydrogen ions(protons) and electrons)

conductors	electronic	metals	
		some inorganic oxides & sulfides	
		semiconductors	n-type
			intrinsic
			p-type
		organic metals	
		conducting polymers	
	mixed	plasmas	
		some solids & solutions	
	ionic	solutions of electrolytes	
		molten salts	
		solid ionic conductors	
		doped crystals	

Illustration 4.2, 4.3, 4.4, 4.5

Polarization

Voltammogram: historical one vs. new one
E > 0 → working electrode potential > 0 (positive: right of x-axis)
I > 0 → oxidation at the working electrode

Polarization: the shift in the voltage across a cell caused by the passage of current

Departure of the cell potential from the reversible(or equilibrium or nernstian) potential

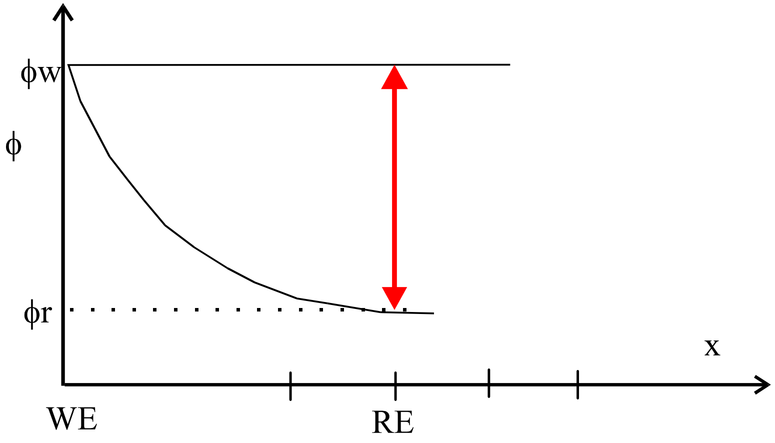
- Ohmic polarization
- Activation polarization
- Concentration polarization

Overvoltage (η, overpotential, **과전압**): the voltage shift caused by each kind of polarization
Extent of potential measured by the overpotential: $\eta = E - E_{eq}$

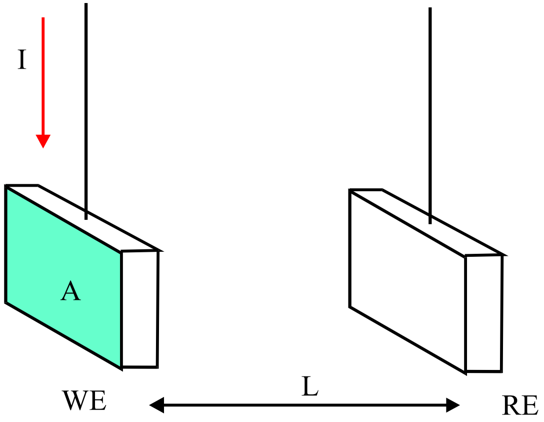
$$\mathbf{E = E_n + \eta_{ohm} + \eta_{act} + \eta_{conc}}$$

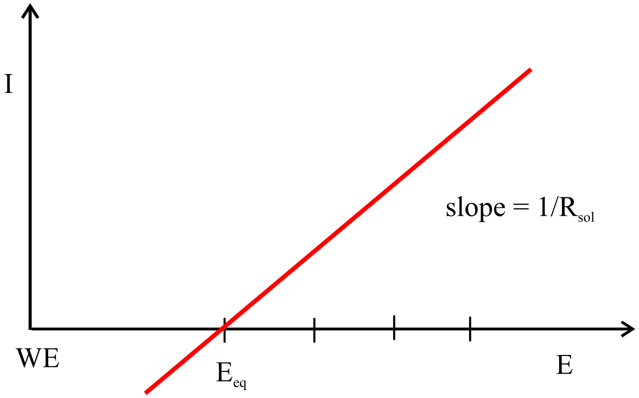
(i) **ohmic polarization**

$\eta_{ohm} = IR_{sol}$, "IR drop"



$R_{sol} = L/\kappa A$





If free of activation & concentration polarization, slope = $1/R_{sol}$

Electrochemistry needs to minimize η_{ohm}

κ (conductivity) $\uparrow \rightarrow \eta_{ohm} \downarrow$ (by adding extra electrolyte: “supporting electrolyte”)

three-electrode system

<u>two-electrode cell vs. three-electrode cell</u>

$$E_{appl} = E + iR_s = E_{eq} + \eta + iR_s$$

IR_s: ohmic drop in the solution (ohmic polarization) → should be minimized → short distance between working and reference electrode & three-electrode cell

Two-electrode cell: iR_s problem due to high current flow

Three-electrode cell: current between WE and auxiliary electrode(or counter electrode)

Potential measurement between WE and RE → almost no current
to reference electrode

→ **Potentiostat, etc electrochemical system: three electrode system**

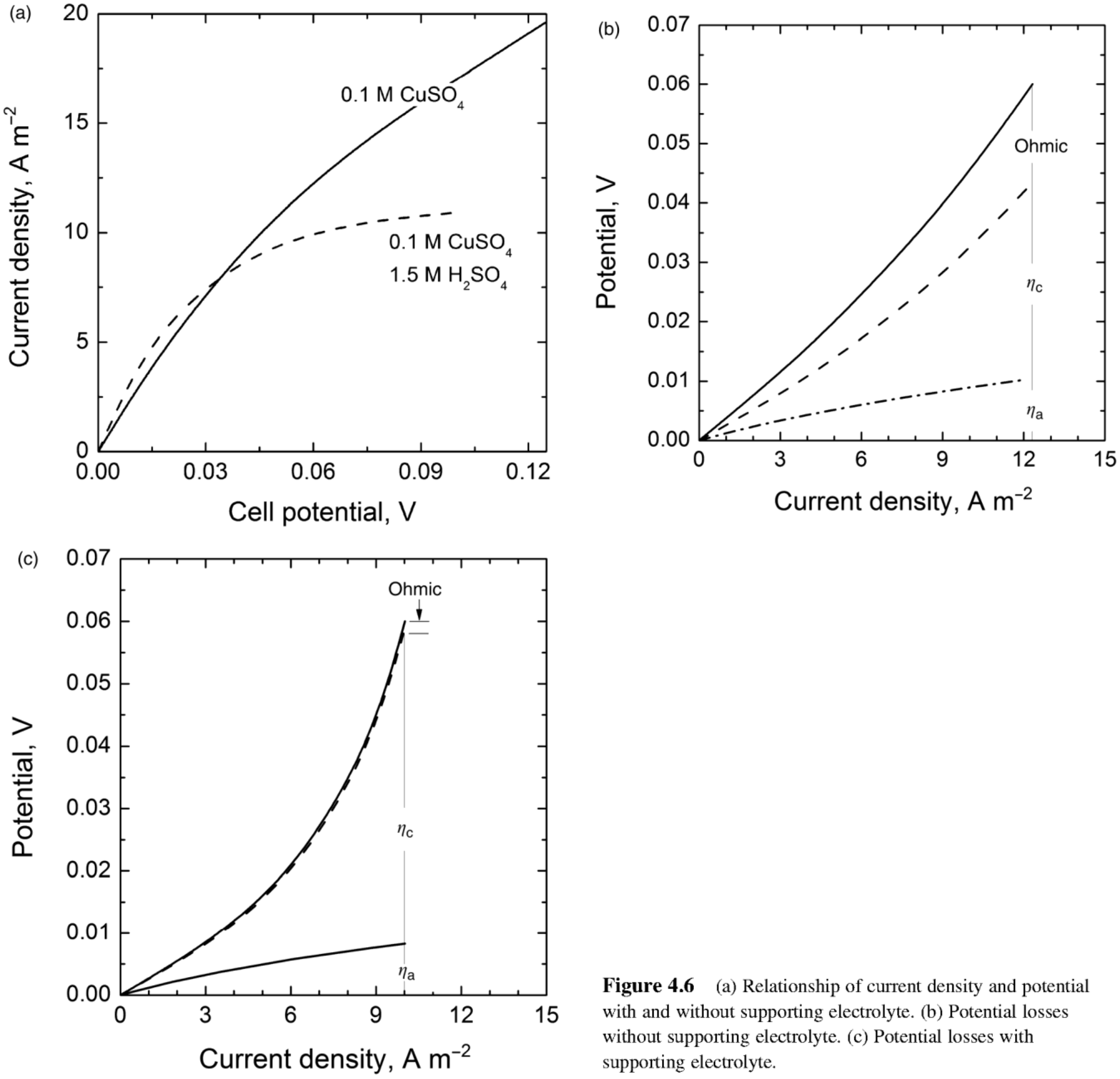
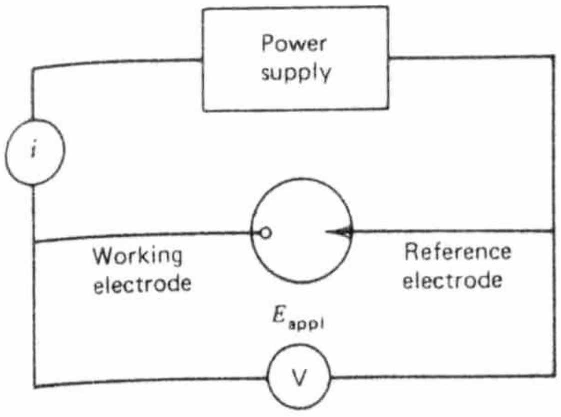
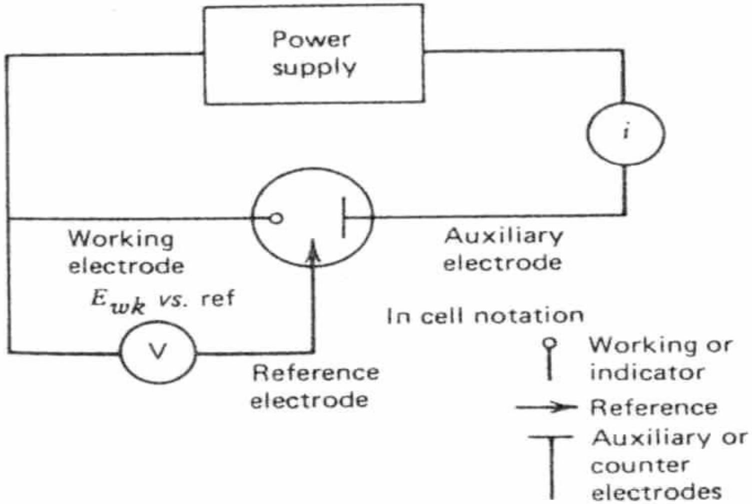


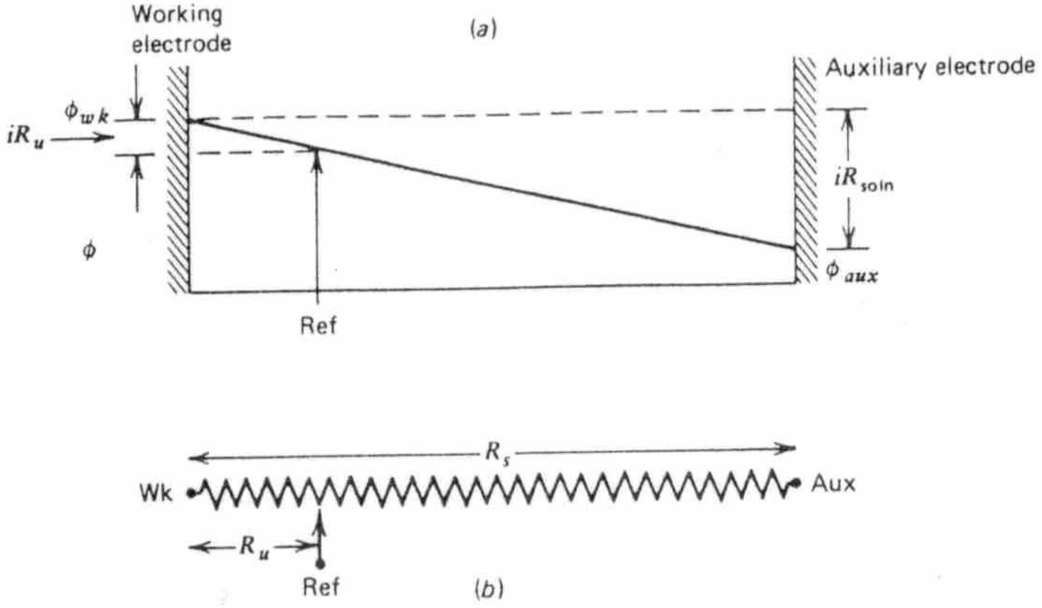
Figure 4.6 (a) Relationship of current density and potential with and without supporting electrolyte. (b) Potential losses without supporting electrolyte. (c) Potential losses with supporting electrolyte.

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

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

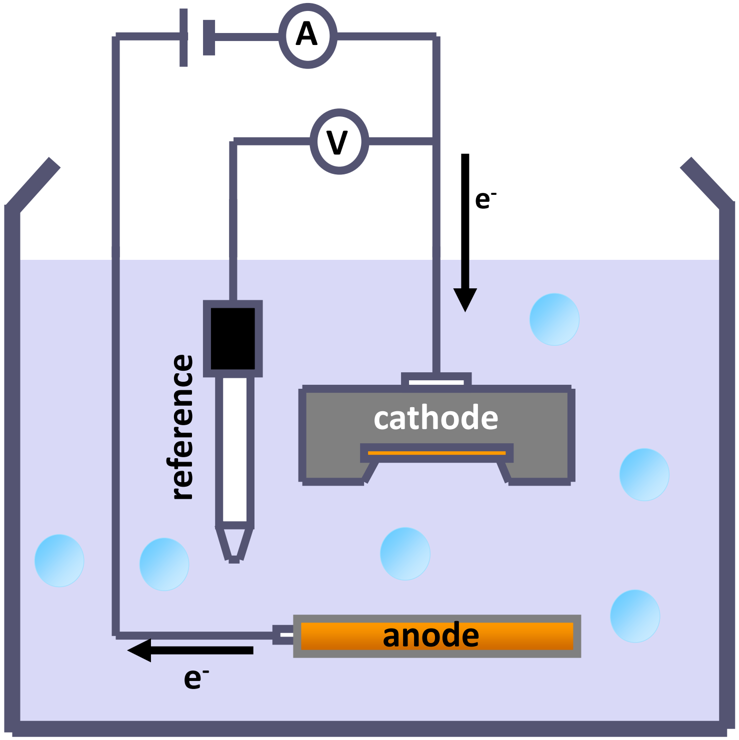




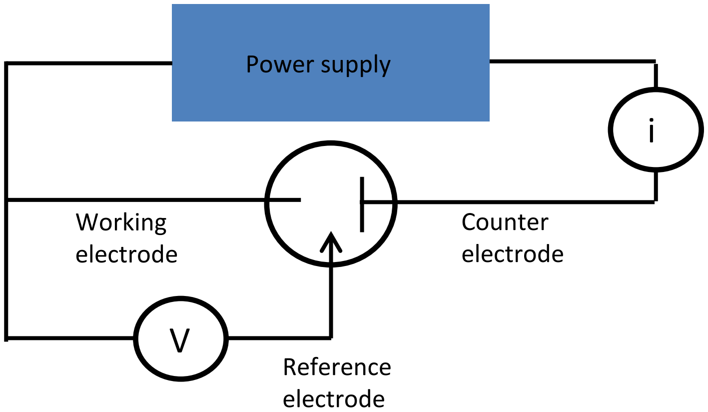


A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001.

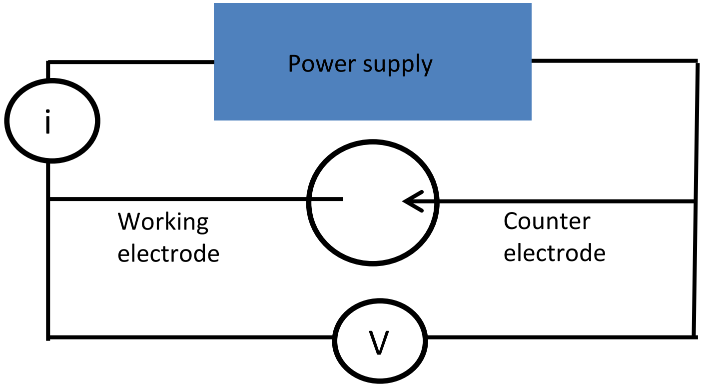
전기화학 측정



- Three electrodes system



- Two electrodes system



그림제공: 권오중 교수(인천대)

(ii) **activation polarization**

slow electrode reaction → activation polarization; slow kinetics $\propto$ activation energy

This can be overcome by increasing the temperature and
by applying extra voltage (activation overvoltage (η_{act}))

(iii) **concentration polarization**

from difference between the electrode surface and bulk concentration

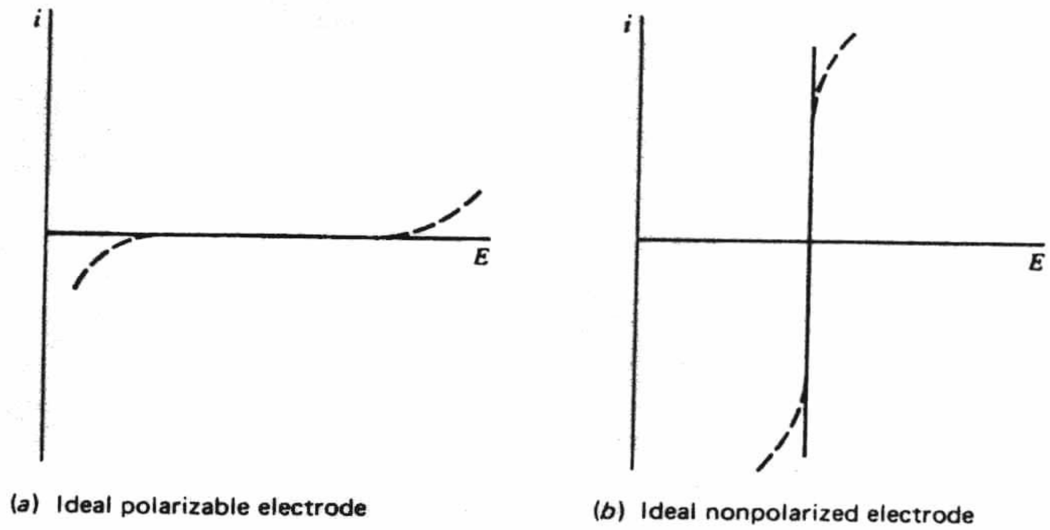
$$R \rightarrow O + ne^-$$

$$\eta_{conc} = E - E_n = (RT/nF)\ln[(c_R^b c_O^s)/c_R^s c_O^b]]$$

Limiting current (i_0) **한계전류**

Ideal polarizable electrode (totally polarized electrode): a very large change in potential upon small current

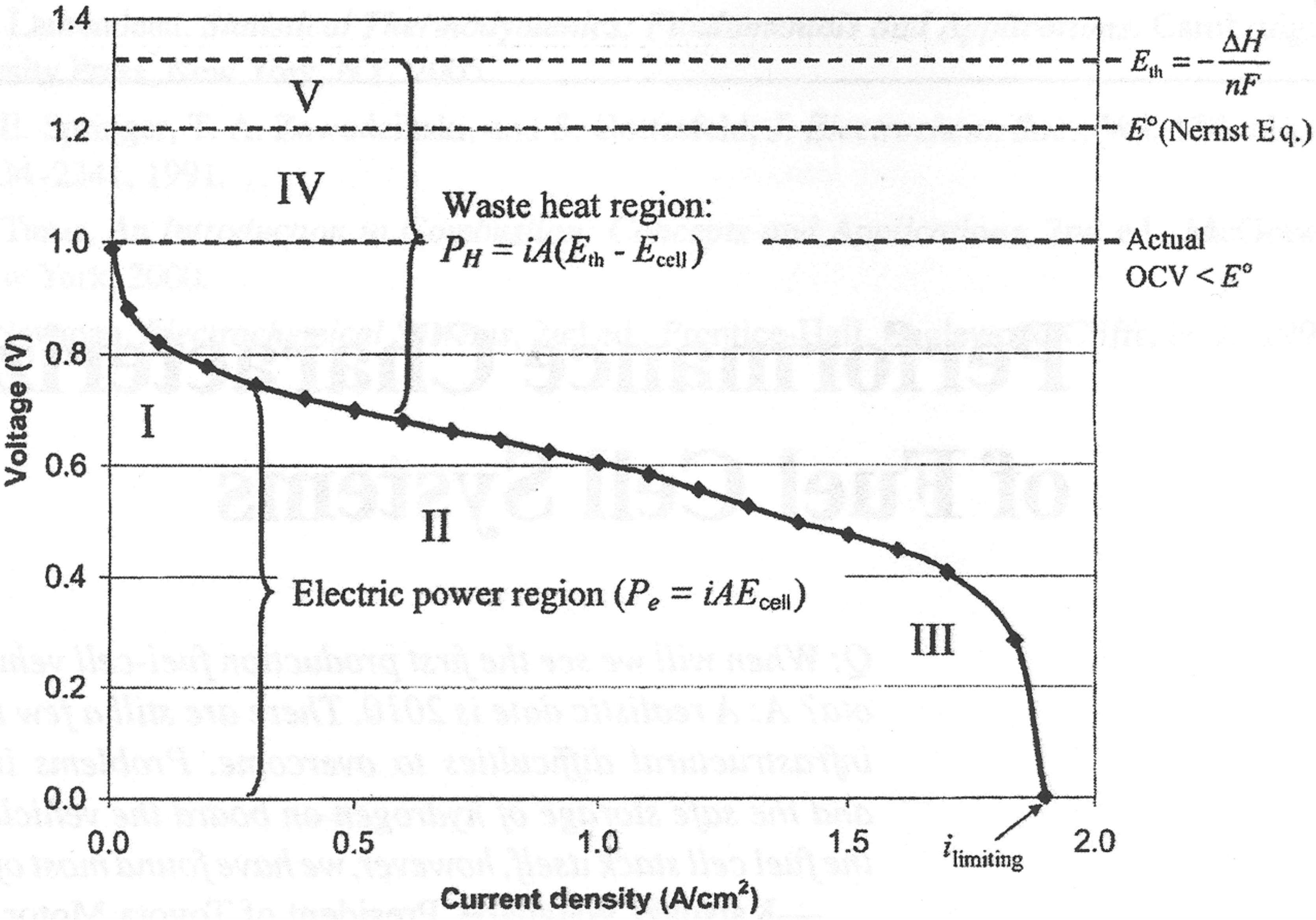
Ideal nonpolarizable electrode: potential does not change upon passage of current (e.g., reference electrode)



(a) Ideal polarizable electrode

(b) Ideal nonpolarized electrode

Fuel cell polarization curve



M. M. Mench, Fuel Cell Engines, Wiley, Fig. 4.1

-5 regions

(i) Region I: activation (kinetic) overpotential at the electrodes
(ii) Region II: ohmic polarization. Electric & ionic conduction loss
(iii) Region III: concentration polarization. Mass transport limitations
(iv) Region IV. Departure from Nernst thermodynamic equilibrium potential; undesired species crossover through electrolyte, internal currents from electron leakage, other contamination or impurity
(v) Region V: the departure from the maximum thermal voltage; a result of entropy change which cannot be engineered

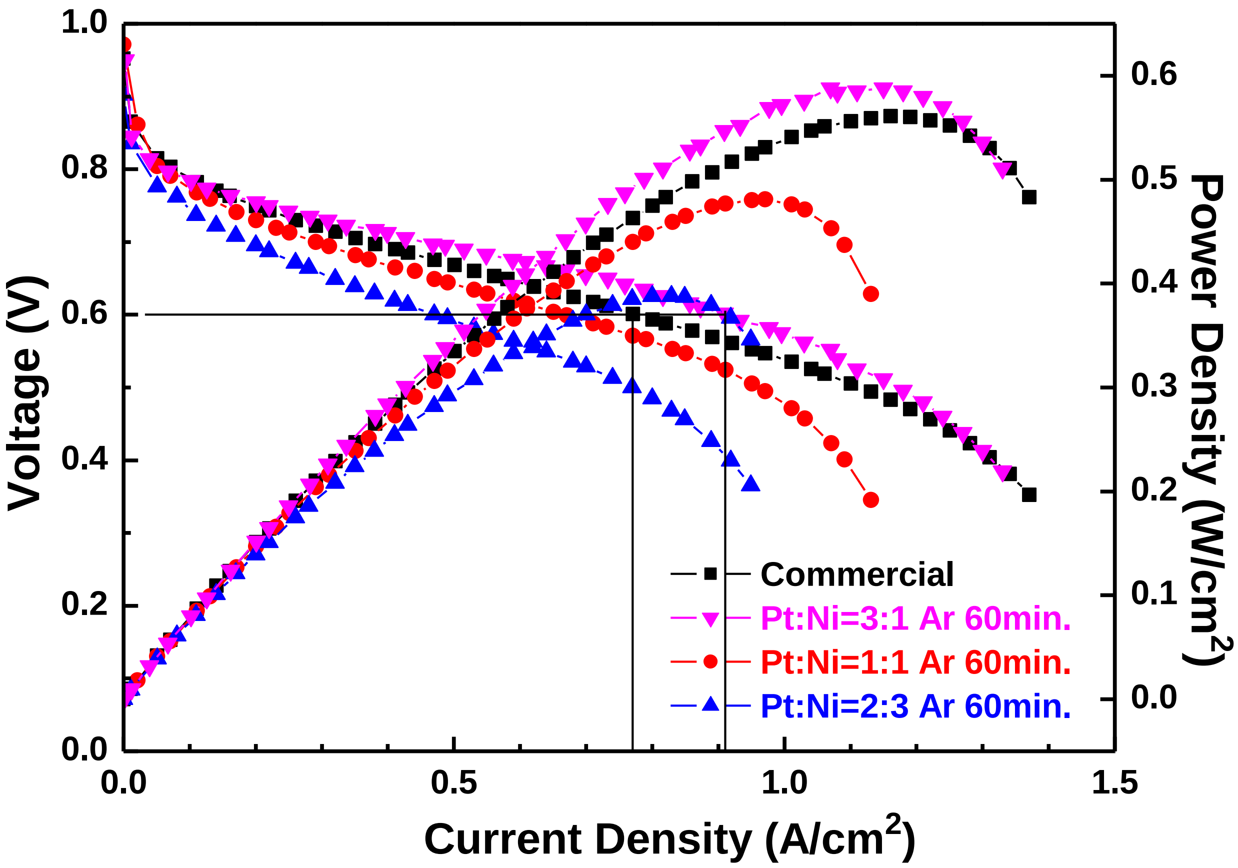
-Regions I, II, III are not discrete → all modes of loss contribute throughout the entire current range

-Heat: current x (thermal voltage – FC voltage)
& electrical generation: cell current x FC voltage

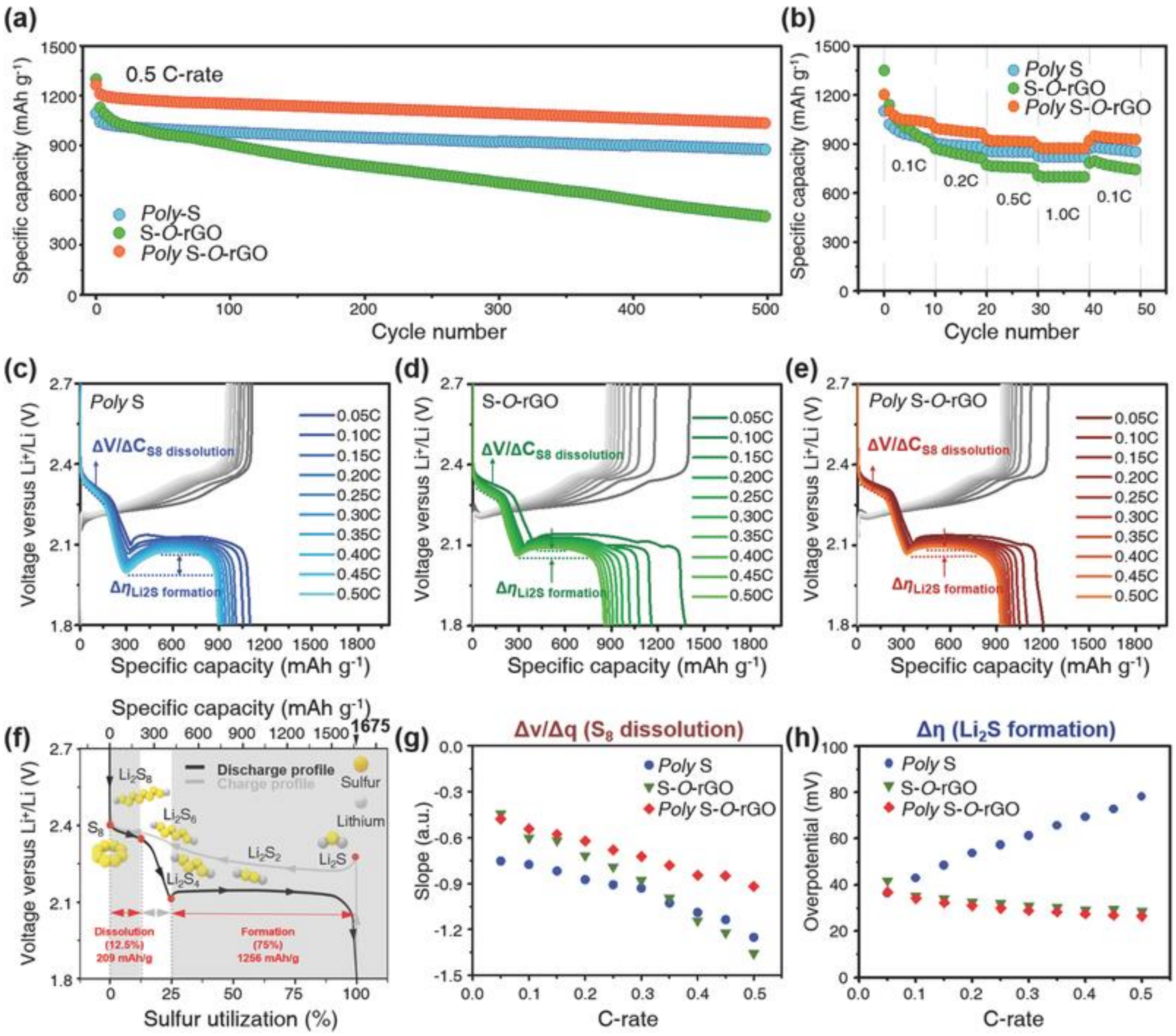
-FC voltage:

$$E_{\text{cell}} = E^{\circ}(T, P) - \eta_{a,a} - |\eta_{a,c}| - \eta_r - \eta_{m,a} - |\eta_{m,c}| - \eta_x \qquad (4.1)$$

I–V Curves in fuel cell



I–V Curves in battery



I-V curves in solar cell