

## 4. Electrode Processes

### Learning subject

1. Working electrode
2. Reference electrode
3. Polarization

### Learning objective

1. Understanding the principle of electrode potential
2. To select reference electrode
3. Understanding three kind of polarizations

# 1. Working electrode

## Electrodes

Working electrode(WE): electrode of interest

Reference electrode(RE): second electrode, measure potential of WE with respect to RE

Electrode potential  $E = E_{\text{work}} - E_{\text{ref}}$

## Reference electrodes

SHE (standard hydrogen electrode) or NHE(normal hydrogen electrode):  
universally accepted standard

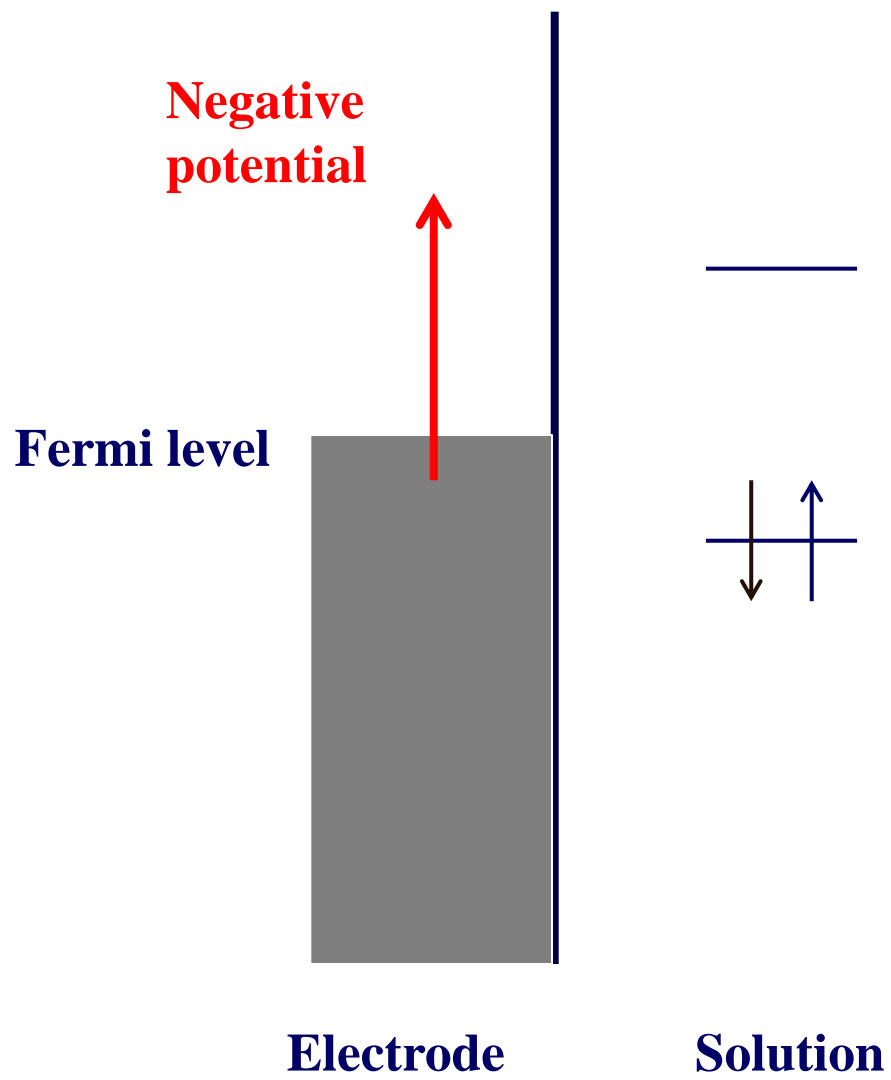


## Electrode potential

Controlling potential of the working electrode with respect to the reference →  
controlling the energy of the electrons within the working electrode

More negative potential → energy of electrons is raised → reach a level to occupy vacant states (LUMO) on species in the electrolyte → flow of electrons from electrode to solution (a reduction current)

More positive potential → electron flow from solution (HOMO) to electrode (oxidation current)



# Applying potential from its equilibrium (or its zero-current)

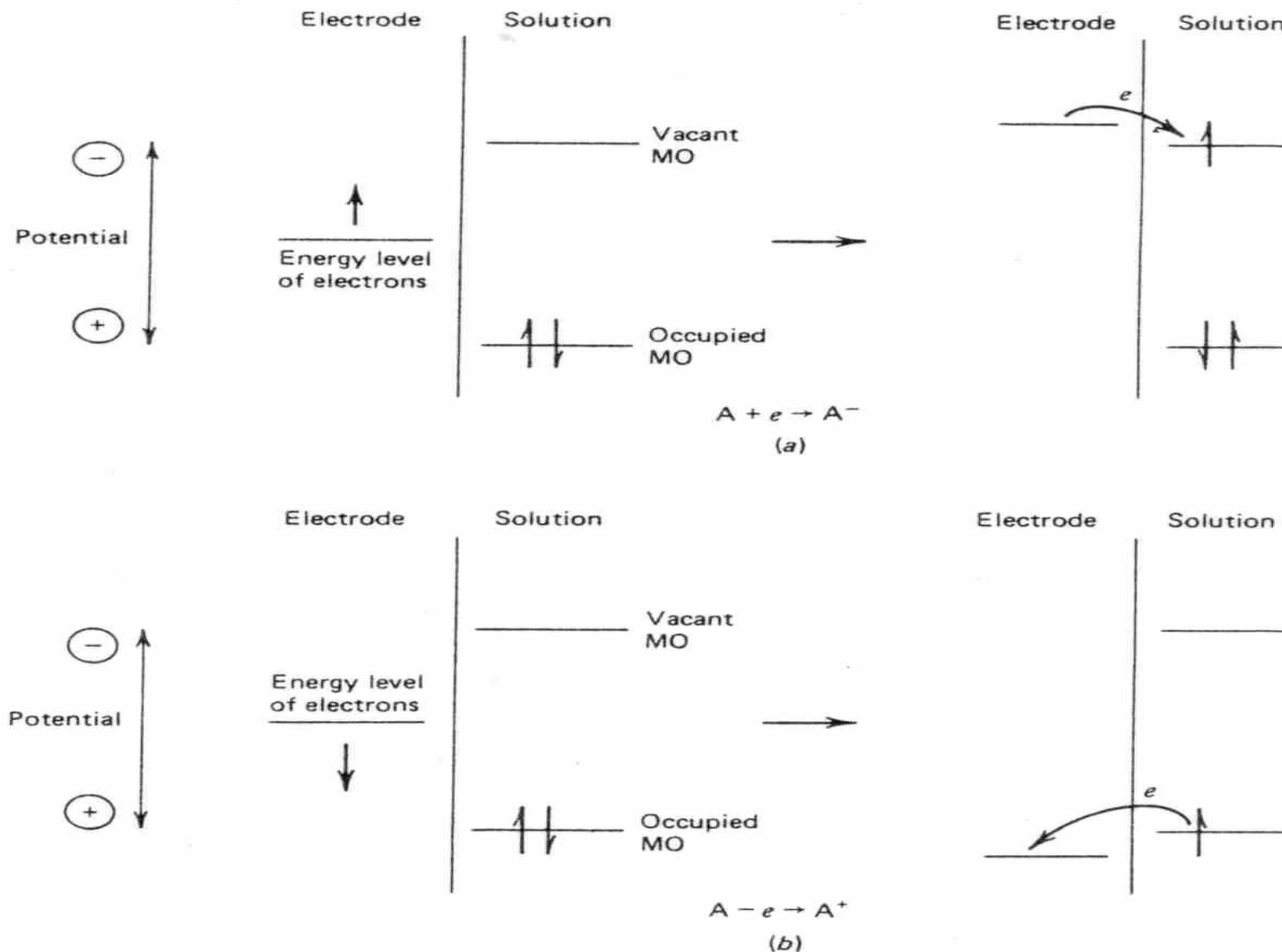
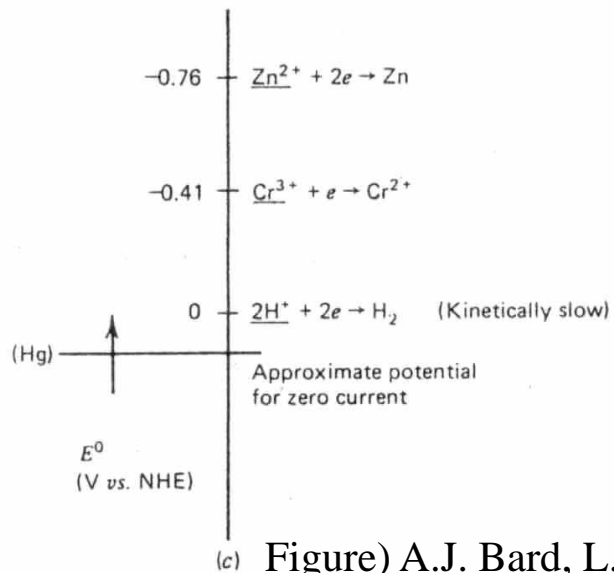
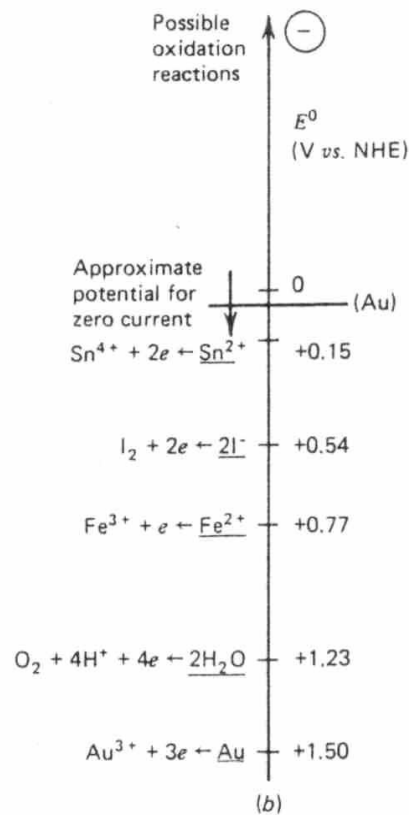
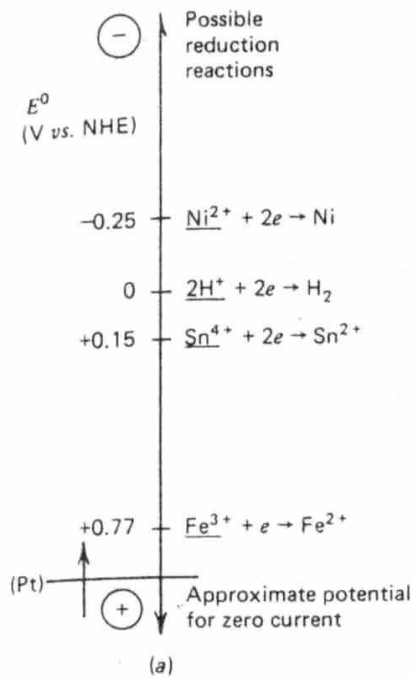


Figure) A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001.

- Potential moved from OCV toward more negative potential: reduced more positive  $E^0$  first
- Potential moved from OCV toward more positive potential: oxidized more negative  $E^0$  first
- consider slow kinetics: slow hydrogen evolution in Hg  $\rightarrow$   $\text{Cr}^{3+}$  reduction first in Figure (c)



(c) Figure) A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001.

## The role of working electrode

Working electrode can act;

- (i) as only a source (for reduction) or a sink (for oxidation) of electrons transferred to or from species in electrolyte (e.g., C, Au, Pt, Hg) or can
- (ii) take part in the electrode reaction, as in dissolution of a metal M ( $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ )



## **Faradaic and nonfaradaic electrode processes**

Faradaic process: charges (e.g., electrons) are transferred across the electrode-electrolyte interface. Electron transfer causes oxidation and reduction to occur: governed by Faraday's law (the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed) → “charge transfer electrode”

Nonfaradaic process: no charge transfer reactions occur because of thermodynamically and kinetically unfavorable. Adsorption/desorption can occur. The structure of the electrode-solution interface can change with changing potential or solution composition. Transiently external current can flow.

Both faradaic and nonfaradaic processes occur when electrode reactions take place

# Nonfaradaic processes and the electrode-solution interface

## Capacitance and charge of an electrode

- Interface = capacitor (two metal sheets separated by a dielectric material)

$$q/E = C$$

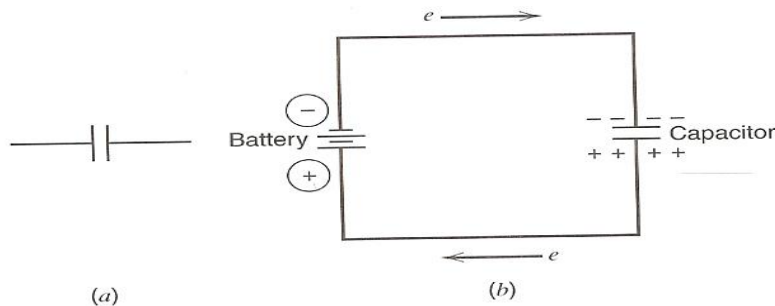
q: charge stored on the capacitor (C, coulomb)

E: potential across the capacitor (V), C: capacitance (F, farad)

- During this charging process, a current (“charging current”) will flow

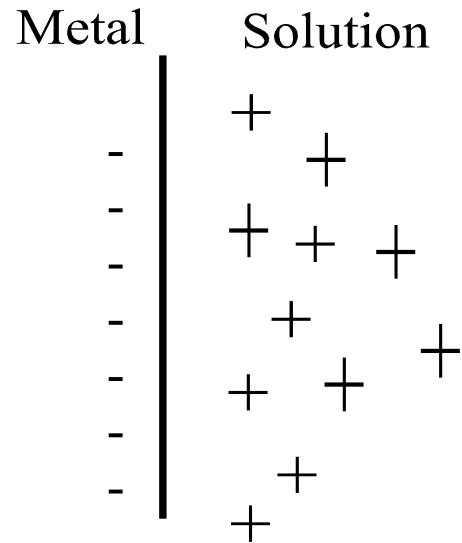
- 2 V battery across 10  $\mu\text{F}$  capacitor

→ current will flow until 20  $\mu\text{C}$  accumulated



**Figure 1.2.1** (a) A capacitor. (b) Charging a capacitor with a battery.

Electrode-solution interface:  $q^M = -q^S$  “electrical double layer”  
 $q^M$ : very thin layer ( $<0.1 \text{ \AA}$ ), charge density ( $\mu\text{C}/\text{cm}^2$ )  $\sigma^M = q^M/A$   
 Typical double-layer capacitance ( $C_d$ ):  $10 \sim 40 \mu\text{F}/\text{cm}^2$



## Electrical double layer

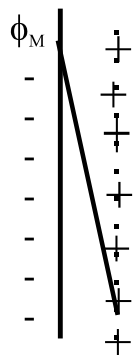
Double layer: several layers

Inner layer (compact, Helmholtz, Stern):

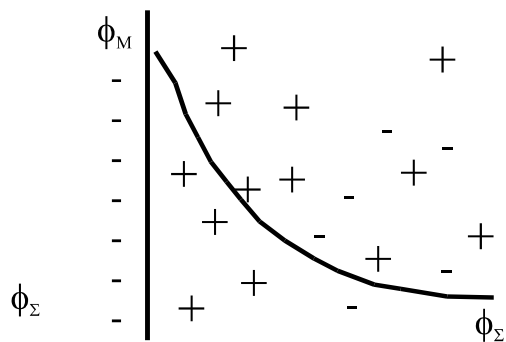
solvent, specifically adsorbed species

Outer Helmholtz plane (OHP): solvated ions

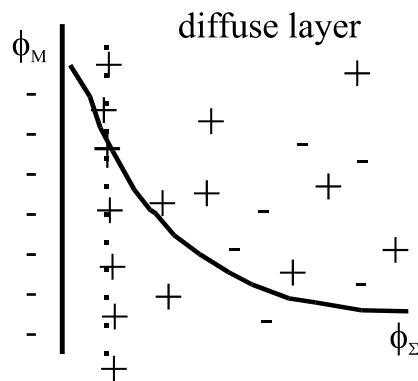
Diffusion layer: extends from OHP to the bulk  
 ( $\sim 100 \text{ \AA}$  in  $>10^{-2} \text{ M}$ )



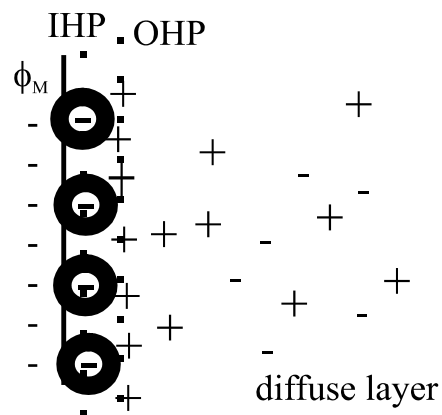
Helmholtz



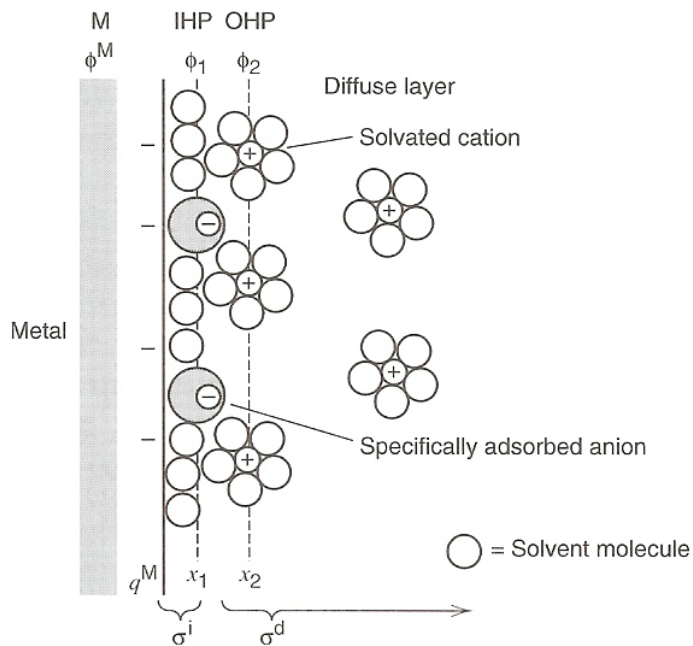
Gouy-Chapman



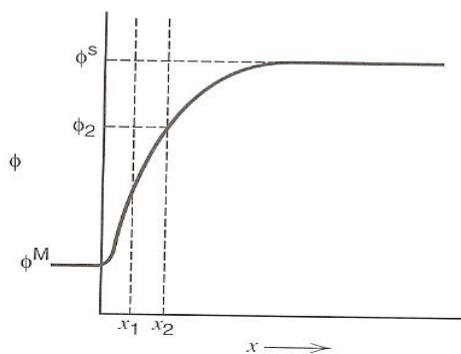
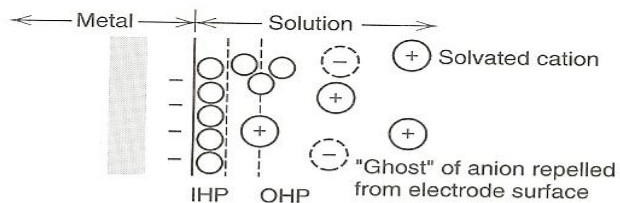
Stern



Grahame

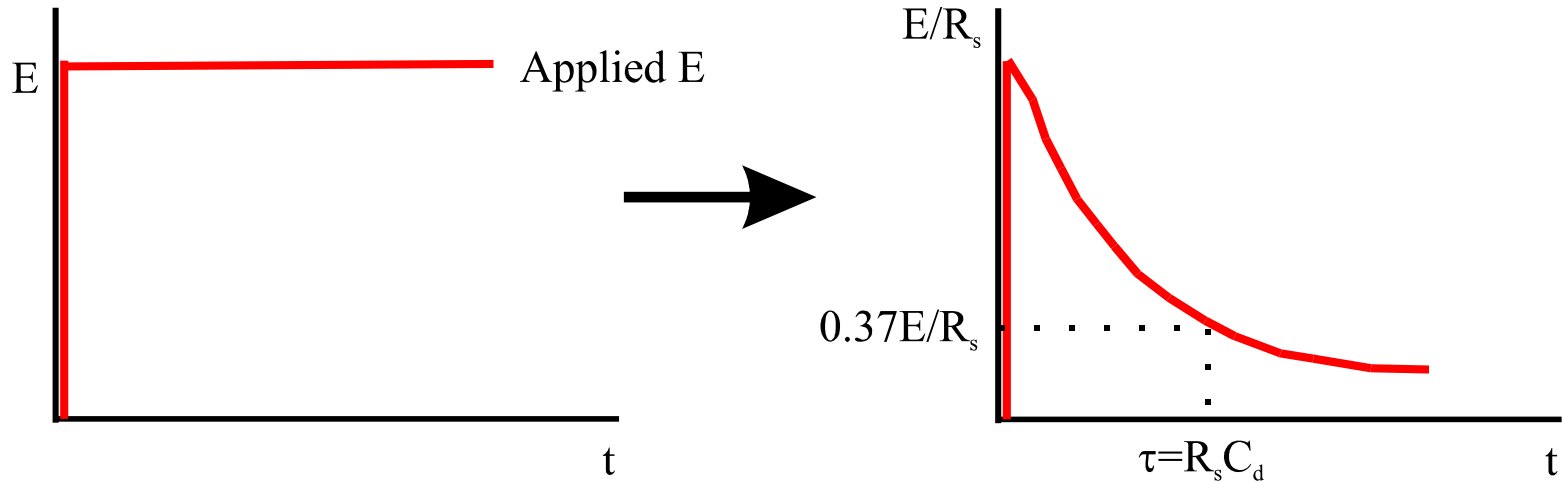


**Figure 1.2.3** Proposed model of the double-layer region under conditions where anions are specifically adsorbed.



**Figure 1.2.4** Potential profile across the double-layer region in the absence of specific adsorption of ions. The variable  $\phi$ , called the *inner potential*, is discussed in detail in Section 2.2. A more quantitative representation of this profile is shown in Figure 12.3.6.

Applying potential to electrode:  
→ current for charging the double layer capacitance



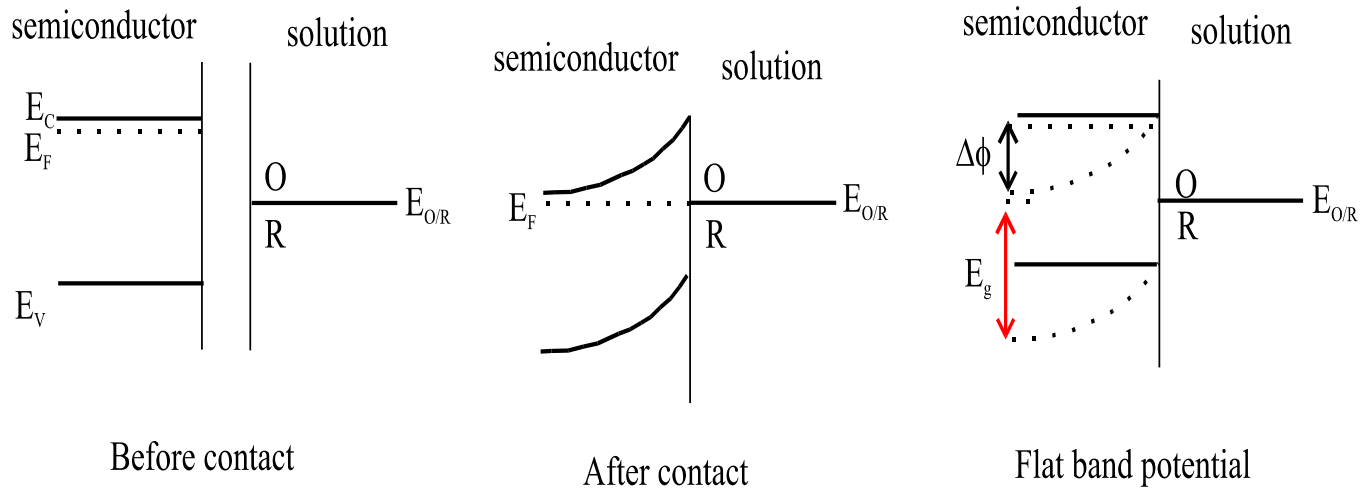
e.g.)  $R_s = 1 \Omega$ ,  $C_d = 20 \mu\text{F}$ ,  $\tau = 20 \mu\text{sec}$  → double layer charging is 95 % complete in  $60 \mu\text{sec}$

Double layer charging process: “non-faradaic process”

## Semiconductor electrode

Semiconductor/electrolyte  $\rightarrow$  space charge region due to space charge capacity,  $C_{sc}$ ,  $0.001 \sim 1 \mu\text{Fcm}^{-2}$ , (cf;  $C_{dl} = 10 \sim 100 \mu\text{Fcm}^{-2}$ )  $\rightarrow$  band bending

n-type SC



when  $E_F$  of SC lies above that in electrolyte  $\rightarrow$  electron flow from SC (positively charged) to electrolyte (negatively charged)  $\rightarrow$  bent upward

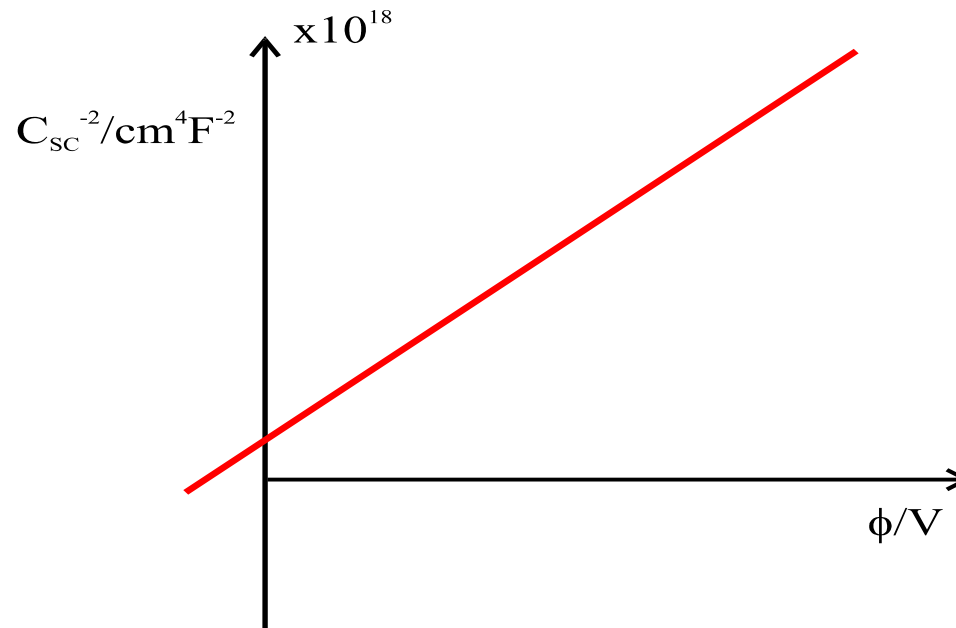
by applying potential of  $\phi_{bulk} = \phi_{surface}$ , band bending & space charge region disappear  $\rightarrow$  “flat band potential ( $\phi_{fb}$  or  $E_{fb}$ )”

space charge capacitance  $C_{sc}$  → Mott-Schottly equation

$$1/C_{sc}^2 = (2/e\epsilon\epsilon_0N)^{1/2}(-\Delta\phi - kT/e)$$

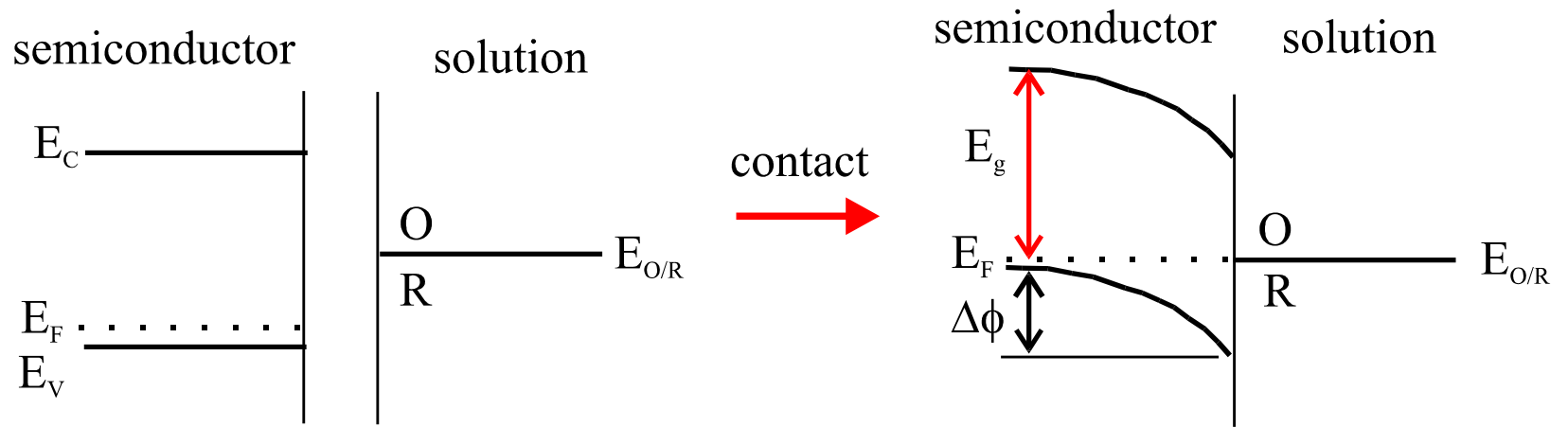
$\epsilon$ : dielectric constant,  $N$ : donor or acceptor densities,  $e$ : quantity of charge,  $-\Delta\phi = E - E_{fb}$

A plot of  $1/C_{sc}^2$  vs. potential  $E$  should be linear →  $E_{fb}$ , doping level  $N$





p-type



## 2. Reference electrode

Electrode potential  $E = E_{\text{work}} - E_{\text{ref}}$

### Reference electrodes

SHE (standard hydrogen electrode) or NHE(normal hydrogen electrode):  
universally accepted standard



SCE (saturated calomel electrode)



Ag/AgCl



Non-Cl system: Hg/Hg<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub>

Nonaqueous system:

- quasireference electrode (QRE):

Ag or Pt wire in organic solvent (e.g., ferrocene/ferrocenium)

$E^0(\text{Zn}^{2+}/\text{Zn})$	-0.763	-1.00	3.7	-3.7
NHE	0	-0.242	4.5	-4.5
SCE	0.242	0	4.7	-4.7
$E^0(\text{Fe}^{3+}/\text{Fe}^{2+})$	0.77	0.53	5.3	-5.3
	<i>E vs. NHE</i> (volts)	<i>E vs. SCE</i> (volts)	<i>E vs. vacuum</i> (volts)	$E_F$ (Fermi energy) (eV)

## Potentials of reference electrodes

$$E(\text{RHE}) = E(\text{NHE}) + 0.05916\text{pH}$$

$$E(\text{SCE}) = E(\text{NHE}) - 0.2444$$

$$E(\text{Ag}/\text{AgCl}) = E(\text{NHE}) - 0.2223$$

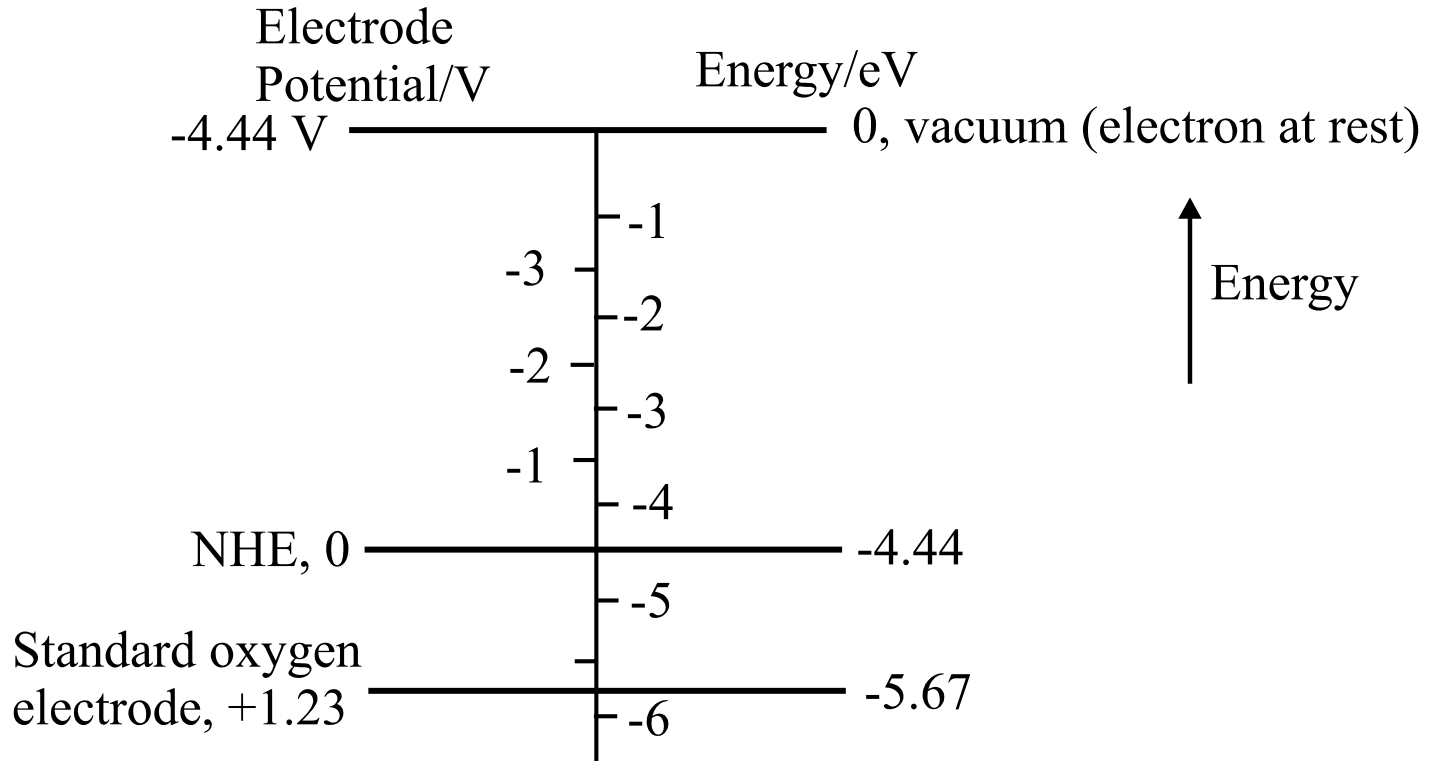
$$E(\text{Ag}/\text{AgCl, sat.KCl}) = E(\text{NHE}) - 0.196$$

$$E(\text{Hg}/\text{HgO 1M KOH}) = E(\text{NHE}) - 0.1100 + 0.05946\text{pH}$$

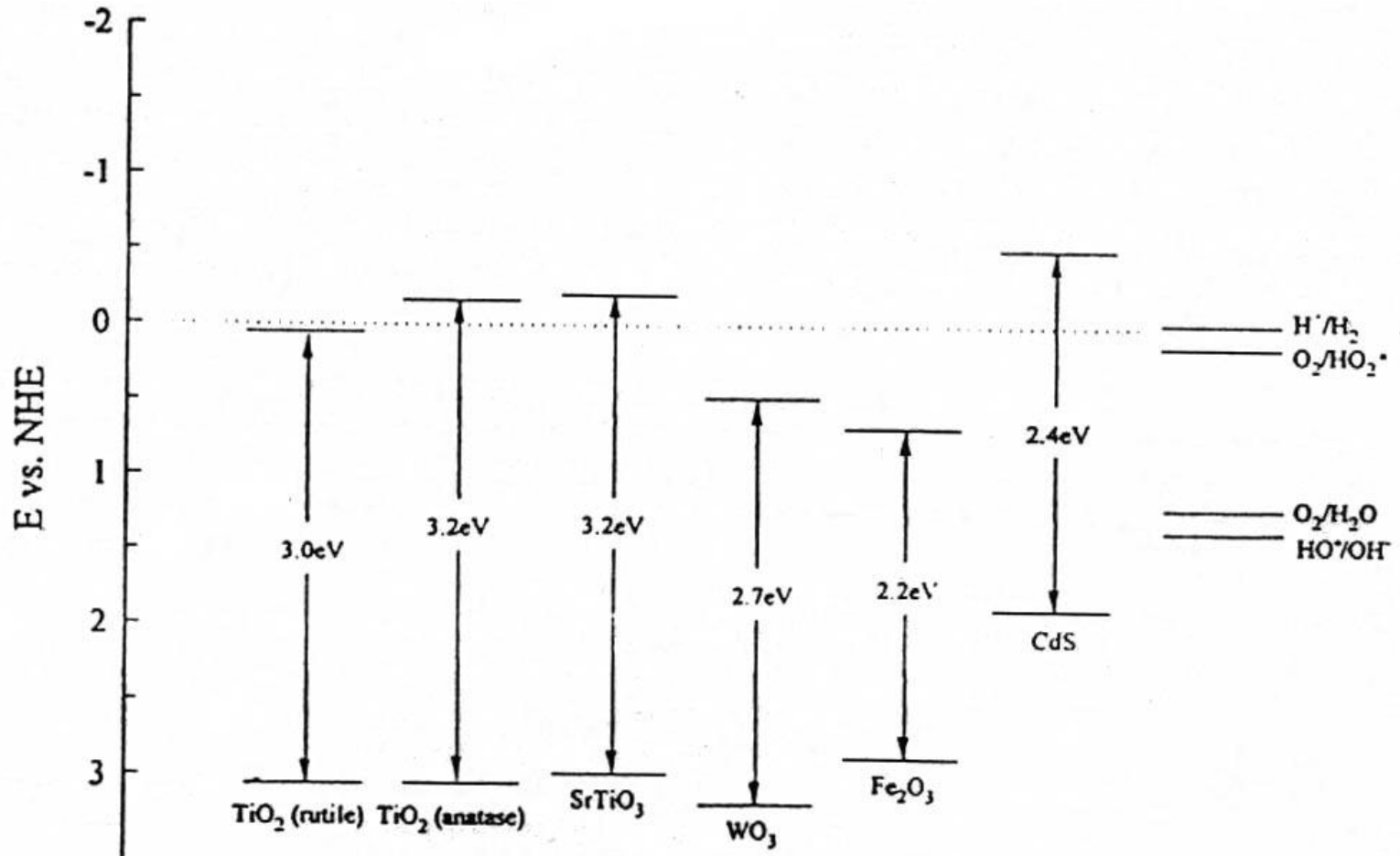
$$E(\text{Hg}/\text{Hg}_2\text{SO}_4) = E(\text{NHE}) - 0.6152$$

	V vs. NHE	V vs. SCE
Hg/HgO, NaOH(0.1 M)	0.926	0.685
Hg/Hg <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> (0.5 M)	0.68	
Hg/Hg <sub>2</sub> SO <sub>4</sub> , K <sub>2</sub> SO <sub>4</sub> (sat'd)	0.64	0.40
Hg/Hg <sub>2</sub> Cl <sub>2</sub> , KCl(0.1 M)	0.3337	
Hg/Hg <sub>2</sub> Cl <sub>2</sub> , KCl(1 M) NCE	0.2801	
Hg/Hg <sub>2</sub> Cl <sub>2</sub> , KCl(sat'd) SCE	0.2412	0.0000
Hg/Hg <sub>2</sub> Cl <sub>2</sub> , NaCl(sat'd) SSCE	0.2360	
Ag/AgCl, KCl(sat'd)	0.197	-0.045
NHE	0.0000	-0.2412

## Potential vs. energy (vs. vacuum)



## Example: Potential vs. energy (vs. vacuum)



### 3. Polarization

**Voltammogram: historical one vs. new one**

$E > 0 \rightarrow$  working electrode potential  $> 0$  (positive: right of x-axis)

$I > 0 \rightarrow$  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

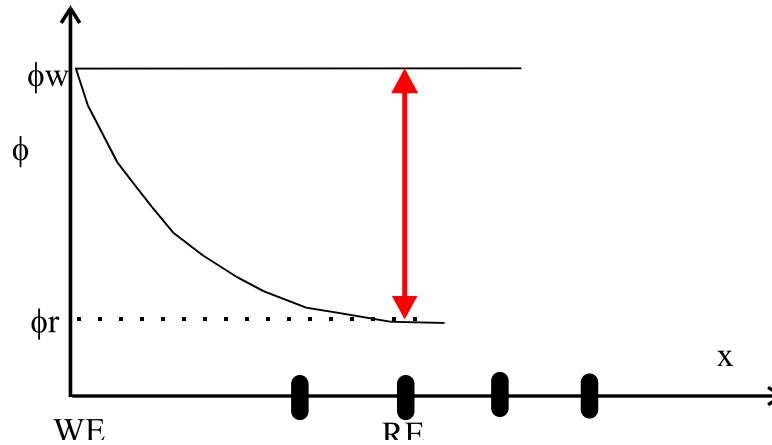
Overvoltage ( $\eta$ ): the voltage shift caused by each kind of polarization

Extent of potential measured by the overpotential:  $\eta = E - E_{eq}$

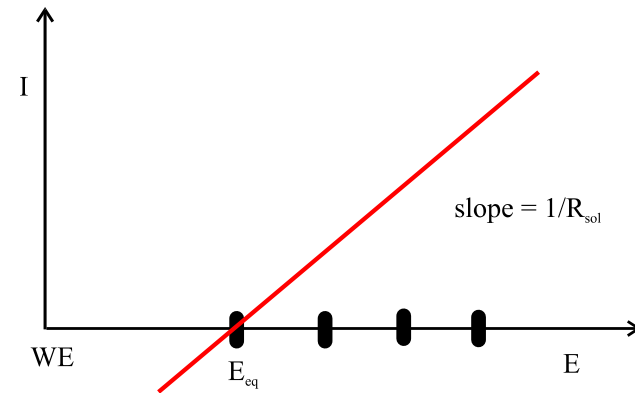
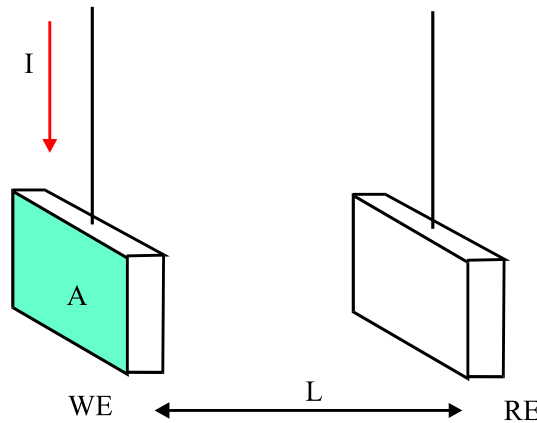
$$E = E_n + \eta_{ohm} + \eta_{act} + \eta_{conc}$$

### (i) ohmic polarization

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



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



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



Electrochemistry needs to minimize  $\eta_{\text{ohm}}$

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

three-electrode system

### two-electrode cell vs. three-electrode cell

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

$iR_s$ : ohmic drop in the solution (ohmic polarization)  $\rightarrow$  should be minimized  $\rightarrow$  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  $\rightarrow$  almost no current to reference electrode

**$\rightarrow$  Potentiostat, etc electrochemical system: three electrode system**

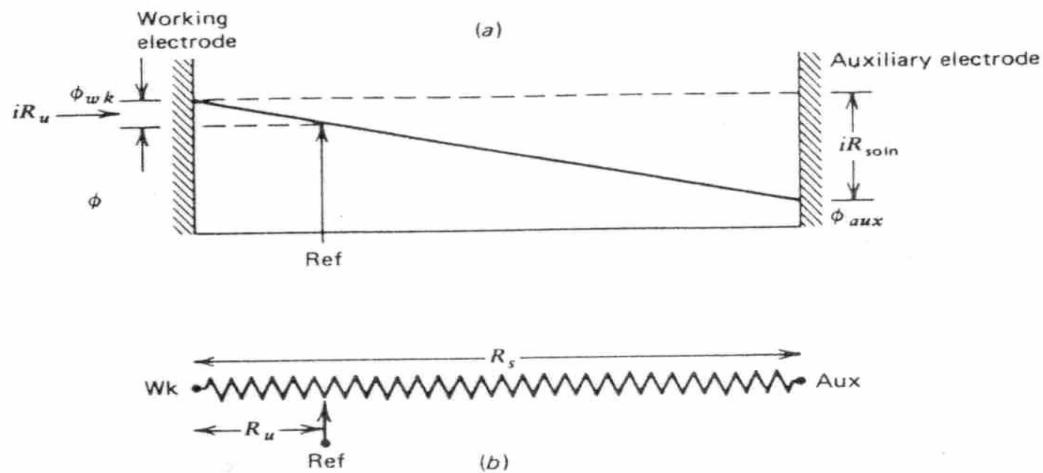
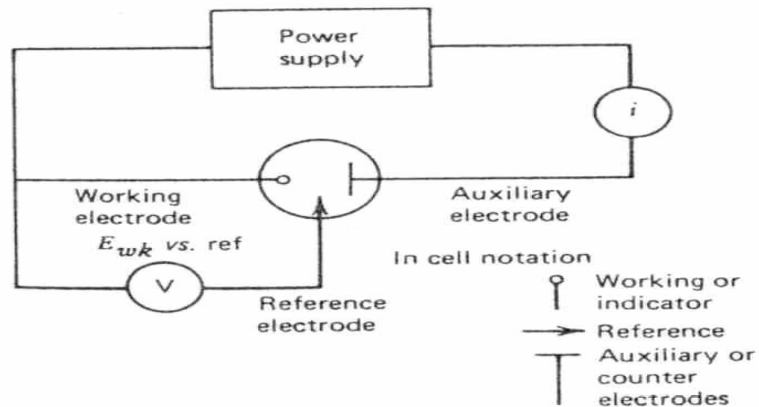
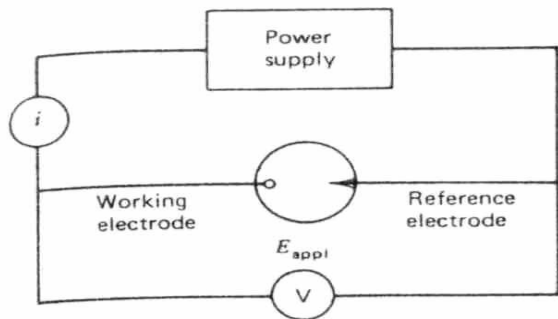


Figure) A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001.

(ii) **activation polarization**

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

**This can be overcome by increasing the temperature and  
by applying extra voltage (activation overvoltage ( $\eta_{act}$ ))**

### (iii) concentration polarization

from difference between the electrode surface and bulk concentration

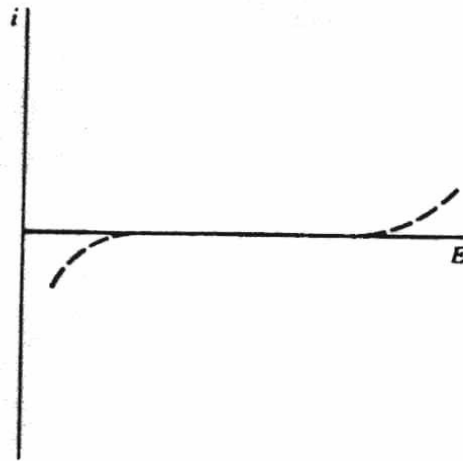


$$\eta_{\text{conc}} = E - E_n = (RT/nF) \ln[(c_R^b c_O^s) / c_R^s c_O^b]$$

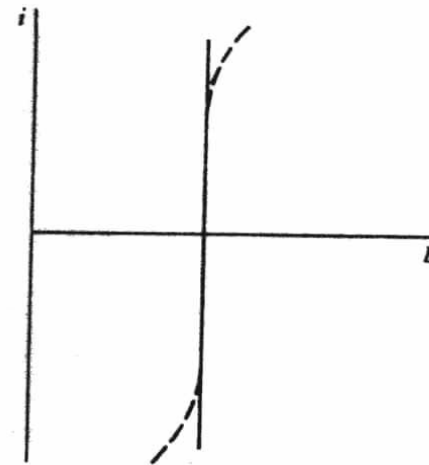
Limiting current

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