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 $E = E_{work} - E_{ref}$

Reference electrodes

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

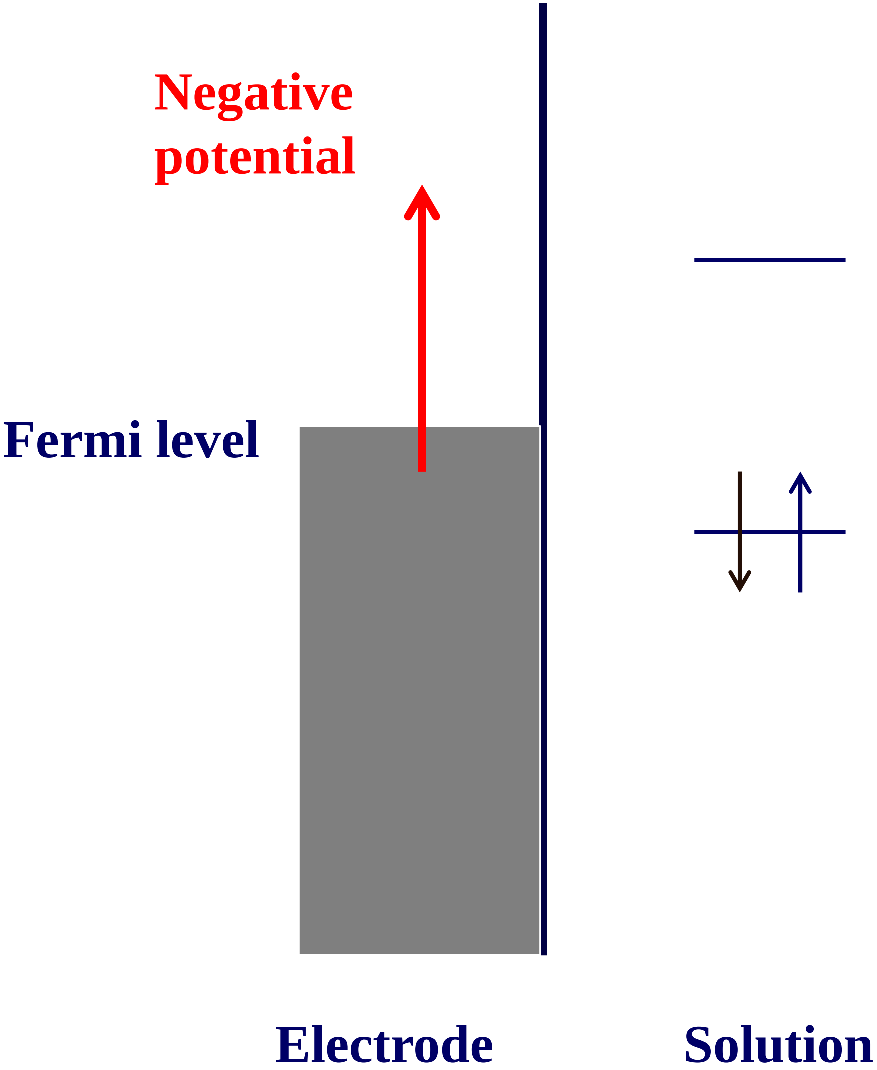
$$H^+(aq, a=1) + e^- = 1/2H_2(g, 10^5\ Pa) \quad E = 0\ V$$

Electrode potential

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

More negitive 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)



Negative potential

Fermi level

Electrode

Solution

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

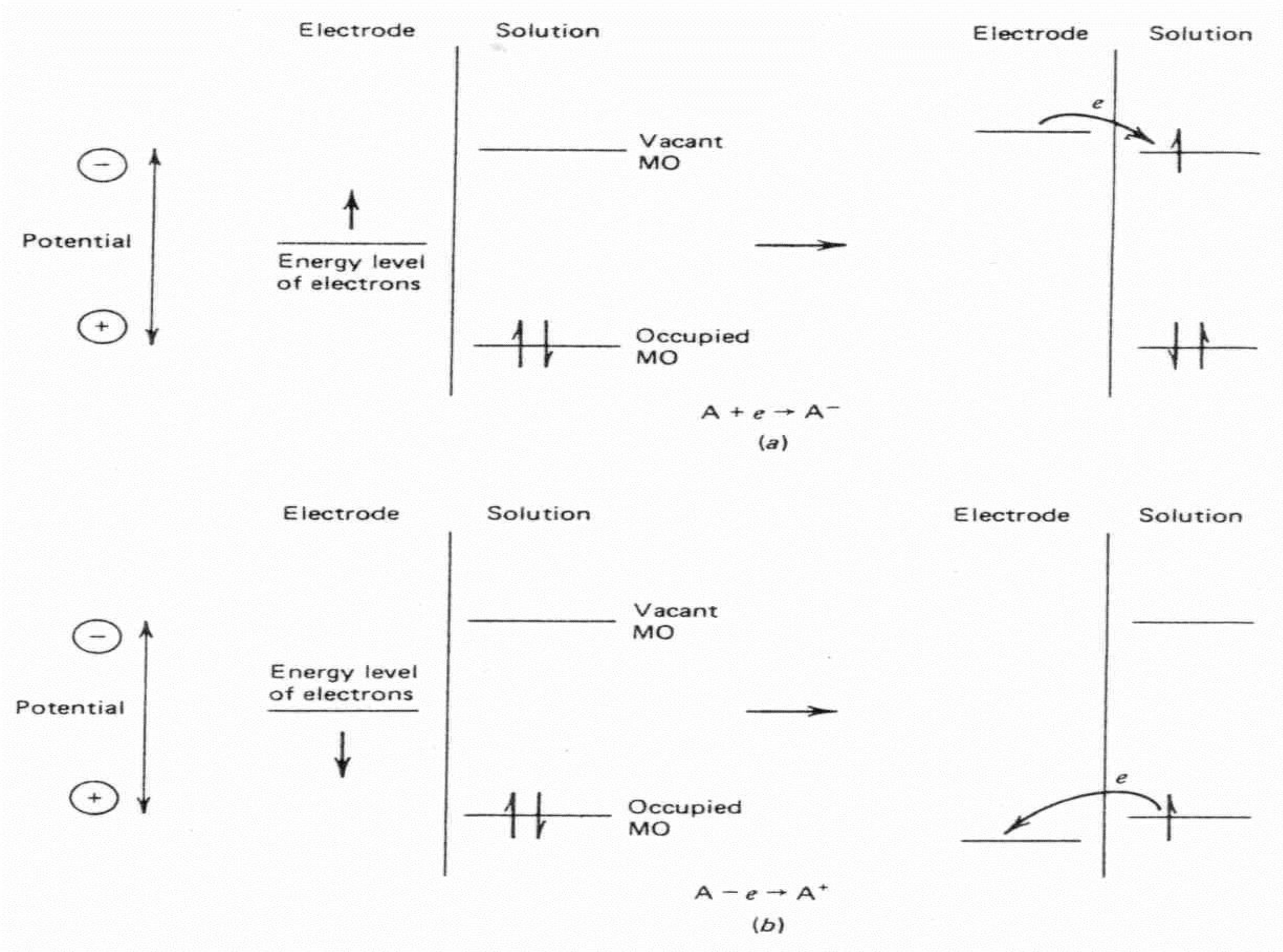


Figure) A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001.

- 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 → Cr^{3+} reduction first in Figure (c)

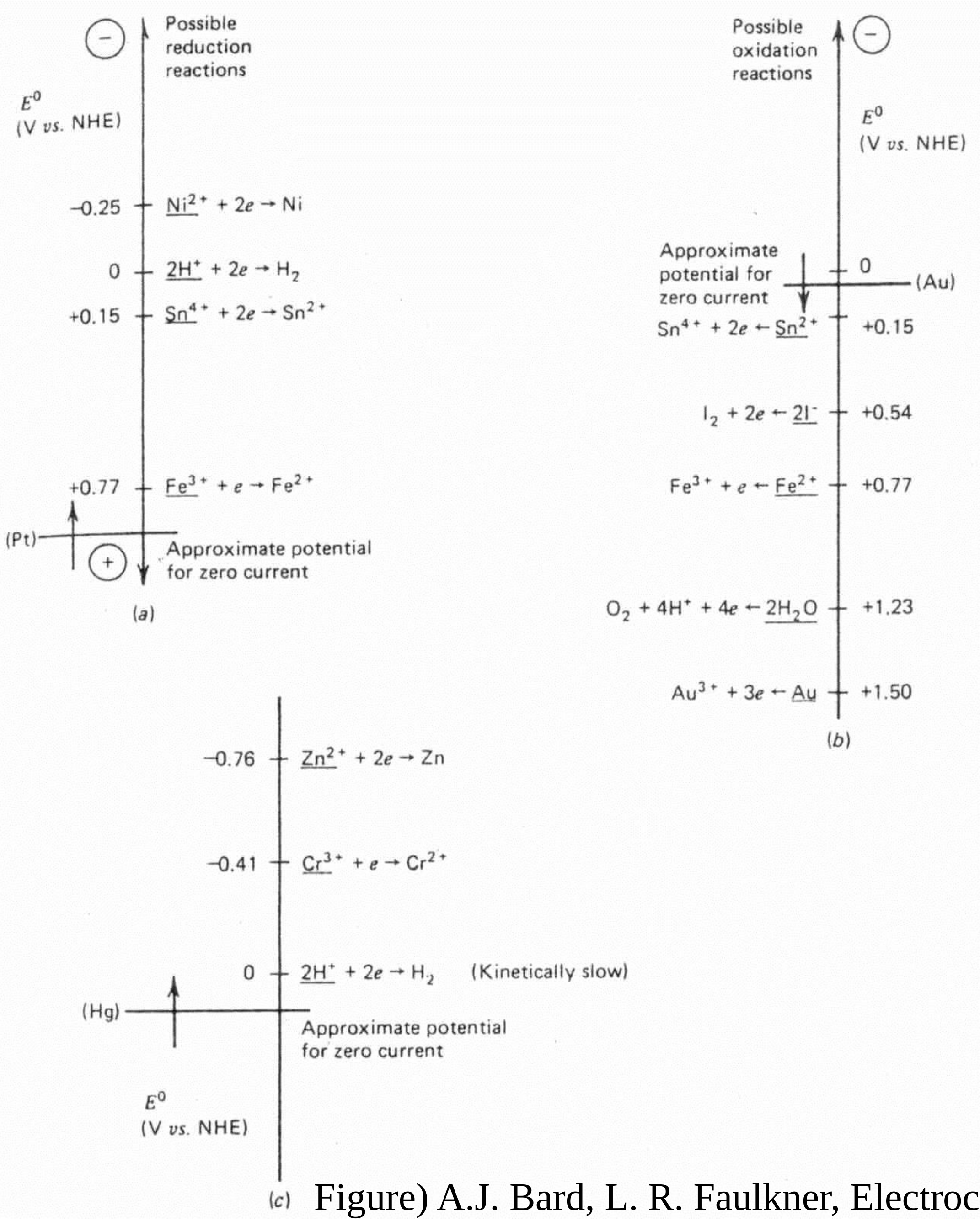


Figure) A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001.

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 ($Zn \rightarrow Zn^{2+} + 2e^-$)

Faradaic and nonfaradaic electrode processes

Faradaic process: charges (e.g., electrons) are transferrred 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 μF capacitor

→ current will flow until 20μC accumulated

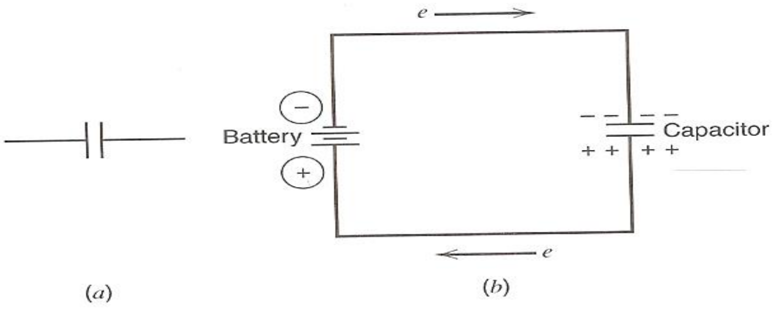
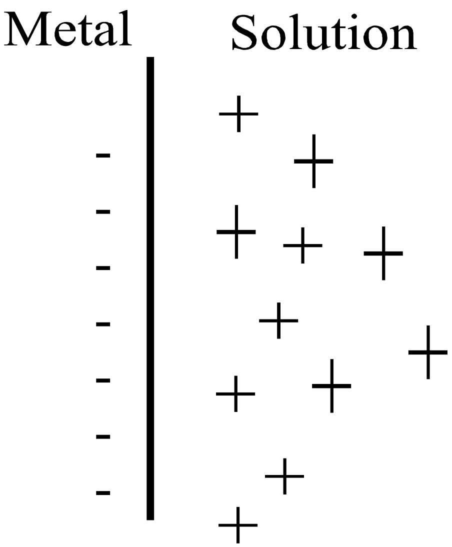


Figure 1.2.1 (*a*) A capacitor. (*b*) Charging a capacitor with a battery.

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

Electrode-solution interface: $q^M = -q^S$ "electrical double layer"
q^M: very thin layer (<0.1 Å), charge density (μC/cm^2) $\sigma^M = q^M/A$
Typical double-layer capacitance (C_d): 10 ~ 40 μF/cm^2



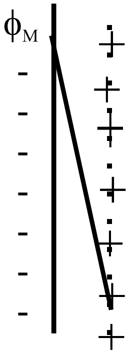
Electrical double layer

Double layer: several layers

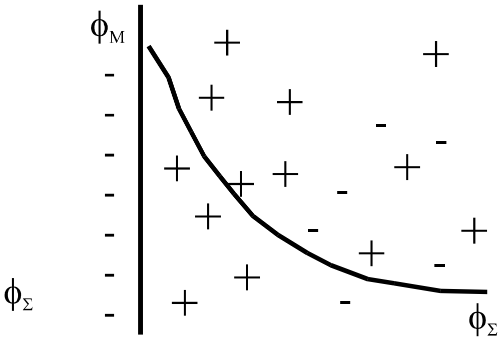
Inner layer (compact, Helmholtz, Stern):
solvent, specifically adsorbed species

Outer Helmholtz plane (OHP): solvated ions

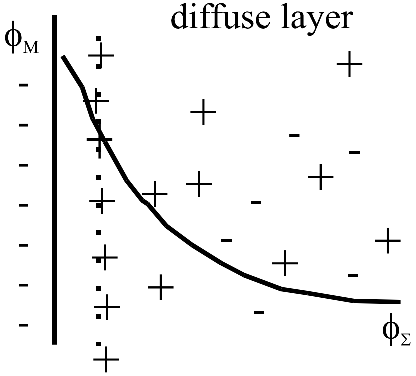
Diffusion layer: extends from OHP to the bulk
(~100 Å in >10^{-2} M)



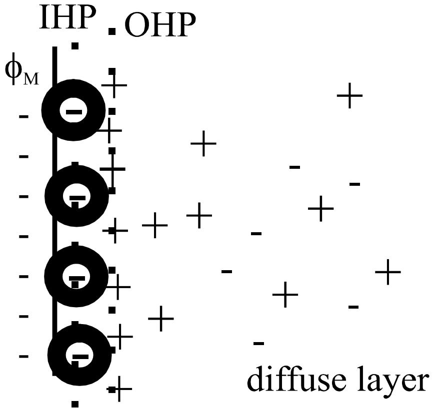
Helmholtz



Gouy-Chapman



Stern



Grahame

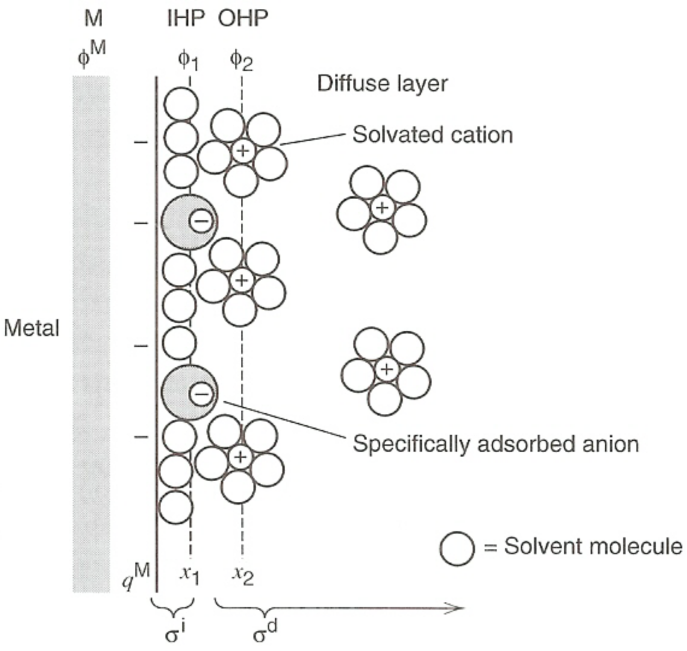
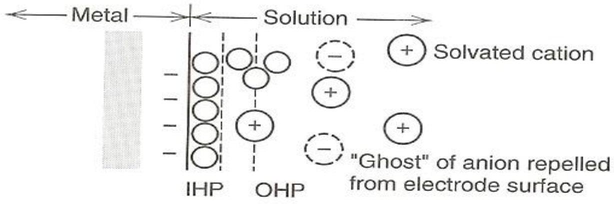


Figure 1.2.3 Proposed model of the double-layer region under conditions where anions are specifically adsorbed.



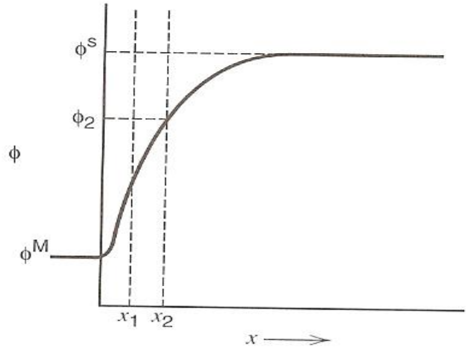
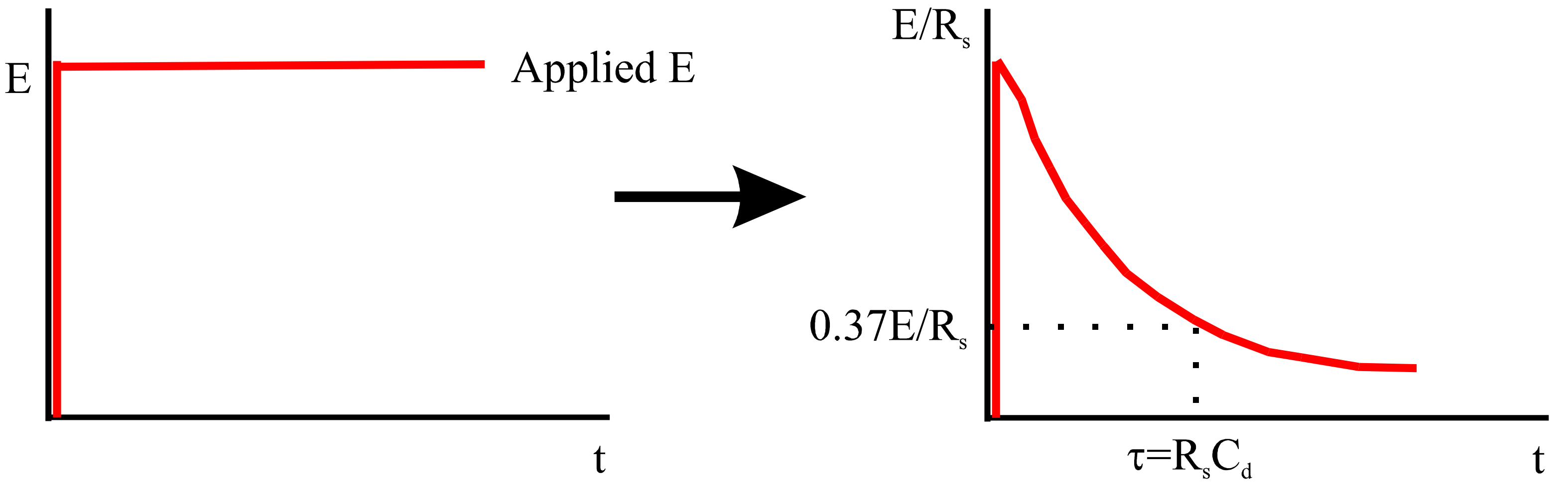


Figure 1.2.4 Potential profile across the double-layer region in the absence of specific adsorption of ions. The variable ϕ, called the *inner potential*, is discussed in detail in Section 2.2. A more quantitative representation of this profile is shown in Figure 12.3.6.

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



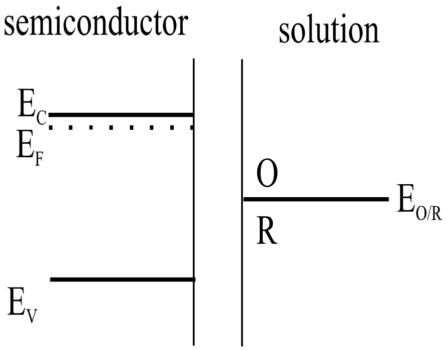
e.g.,) R_s = 1 Ω, C_d = 20 μF, τ = 20 μsec → double layer charging is 95 % complete in 60 μsec

Double layer charging process: “non-faradaic process”

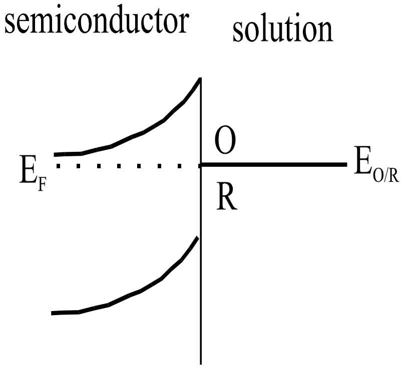
Semiconductor electrode

Semiconductor/electrolyte → space charge region due to space charge capacity, C_{sc}, 0.001 ~ 1 μFcm^{-2}, (cf; C_{dl} = 10 ~ 100 μFcm^{-2}) → band bending

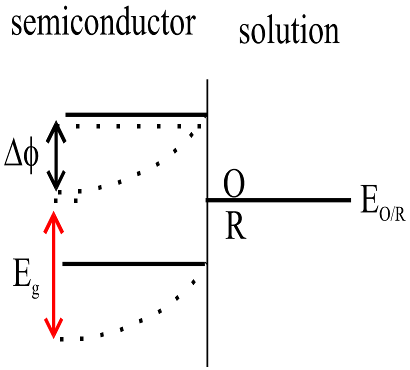
n-type SC



Before contact



After contact



Flat band potential

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

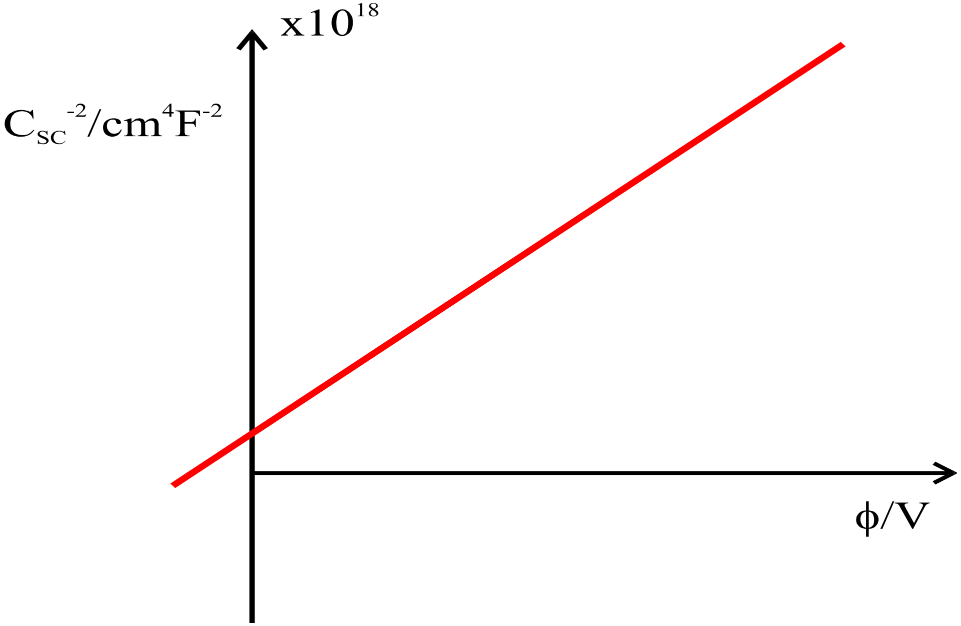
by applying potential of $\phi_{bulk} = \phi_{surface}$, band bending & space charge region disappear → "flat band potential (ϕ_{fb} or E_{fb})"

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

$$1/C_{sc}^{2} = (2/e\varepsilon\varepsilon_0 N)^{1/2}(-\Delta\phi - kT/e)$$

ε: 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



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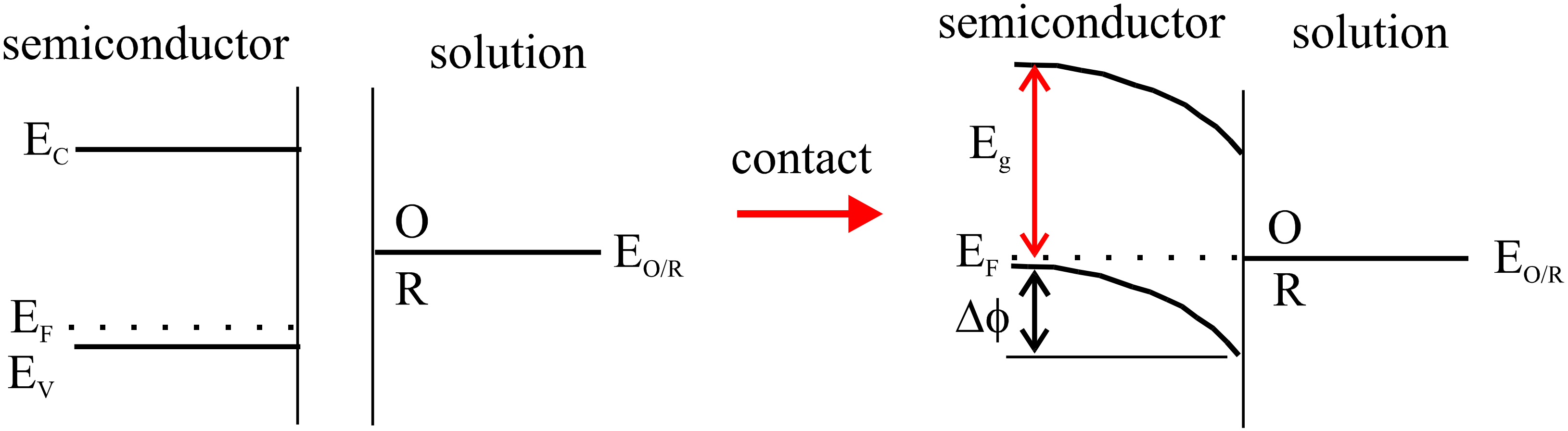

semiconductor
solution
E_C
E_F
E_V
O
R
$E_{O/R}$
contact
semiconductor
solution
E_g
E_F
$\Delta\phi$
O
R
$E_{O/R}$

2. Reference electrode

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

Reference electrodes

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

$$H^+(aq, a=1) + e^- = 1/2H_2(g, 10^5\ Pa) \quad E = 0\ V$$

SCE (saturated calomel electrode)

$$Hg_2Cl_2(s) + 2e^- = 2Hg + Cl^- \quad E_{ref} = 0.244\ V \text{ vs. NHE}$$

Ag/AgCl

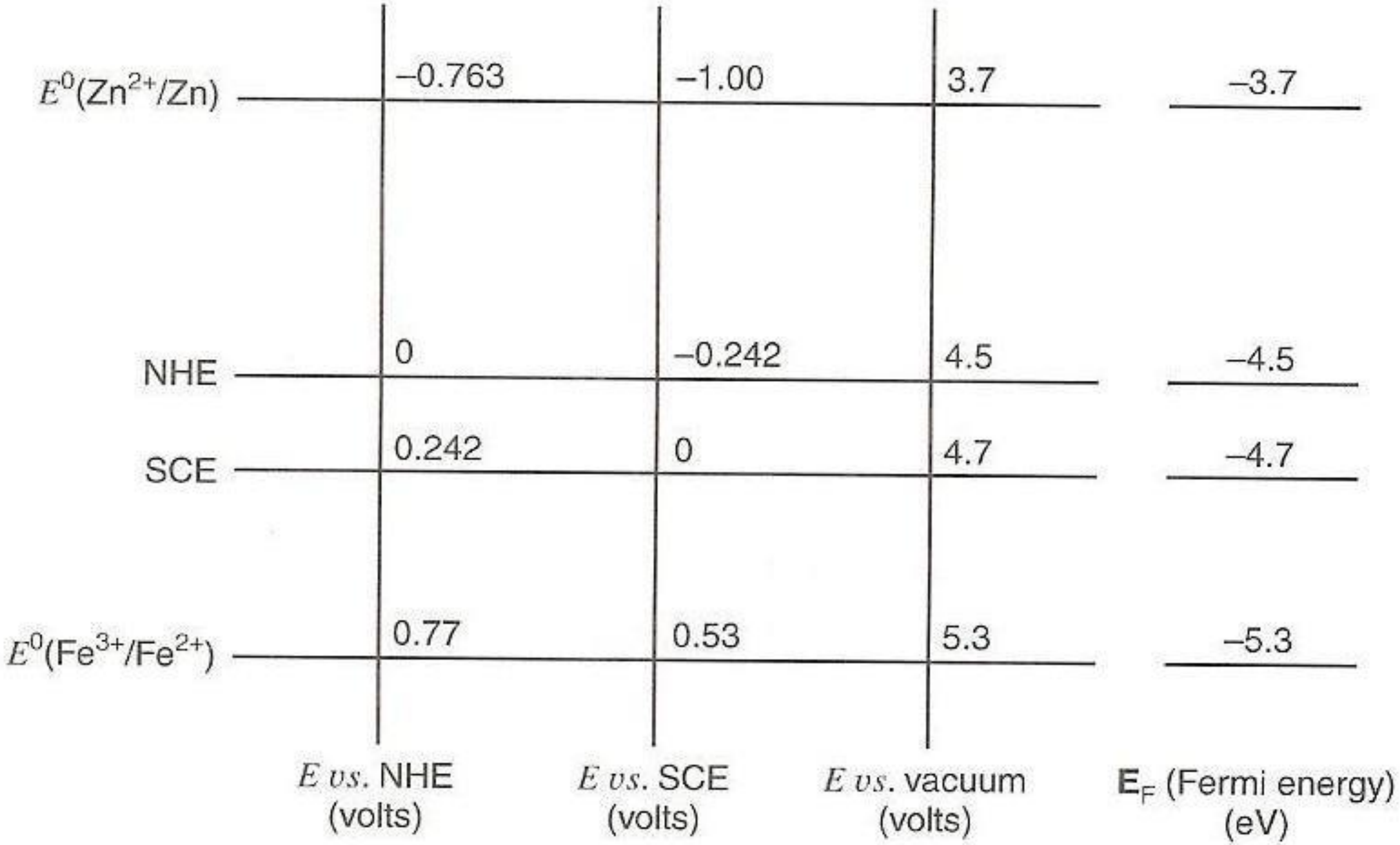
$AgCl(s) + e^- = Ag(s) + Cl^-(aq)$ $E_{ref} = 0.199$ V with saturated KCl

Non-Cl system: $Hg/Hg_2SO_4/K_2SO_4$

Nonaqueous system:

- quasireference electrode (QRE):

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



	E *vs.* NHE (volts)	E *vs.* SCE (volts)	E *vs.* vacuum (volts)	$\mathbf{E}_F$ (Fermi energy) (eV)
$E^0(Zn^{2+}/Zn)$	–0.763	–1.00	3.7	–3.7
NHE	0	–0.242	4.5	–4.5
SCE	0.242	0	4.7	–4.7
$E^0(Fe^{3+}/Fe^{2+})$	0.77	0.53	5.3	–5.3

Potentials of reference electrodes

E(RHE) = E(NHE) + 0.05916pH

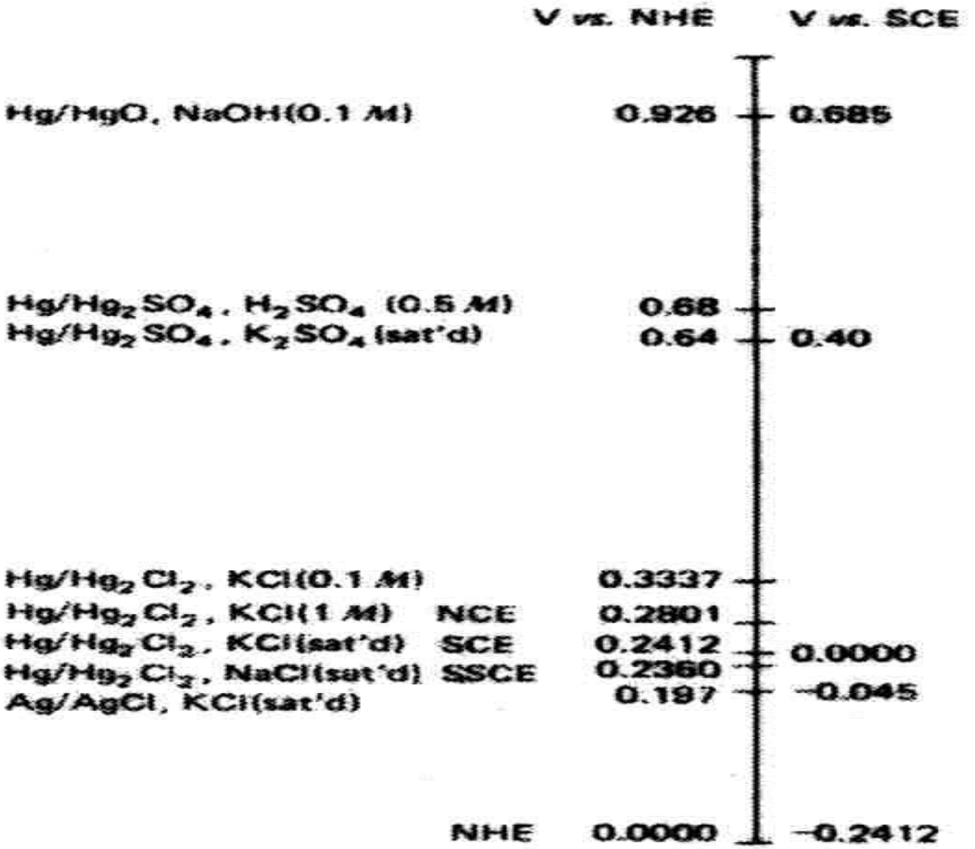
E(SCE) = E(NHE) – 0.2444

E(Ag/AgCl) = E(NHE) – 0.2223

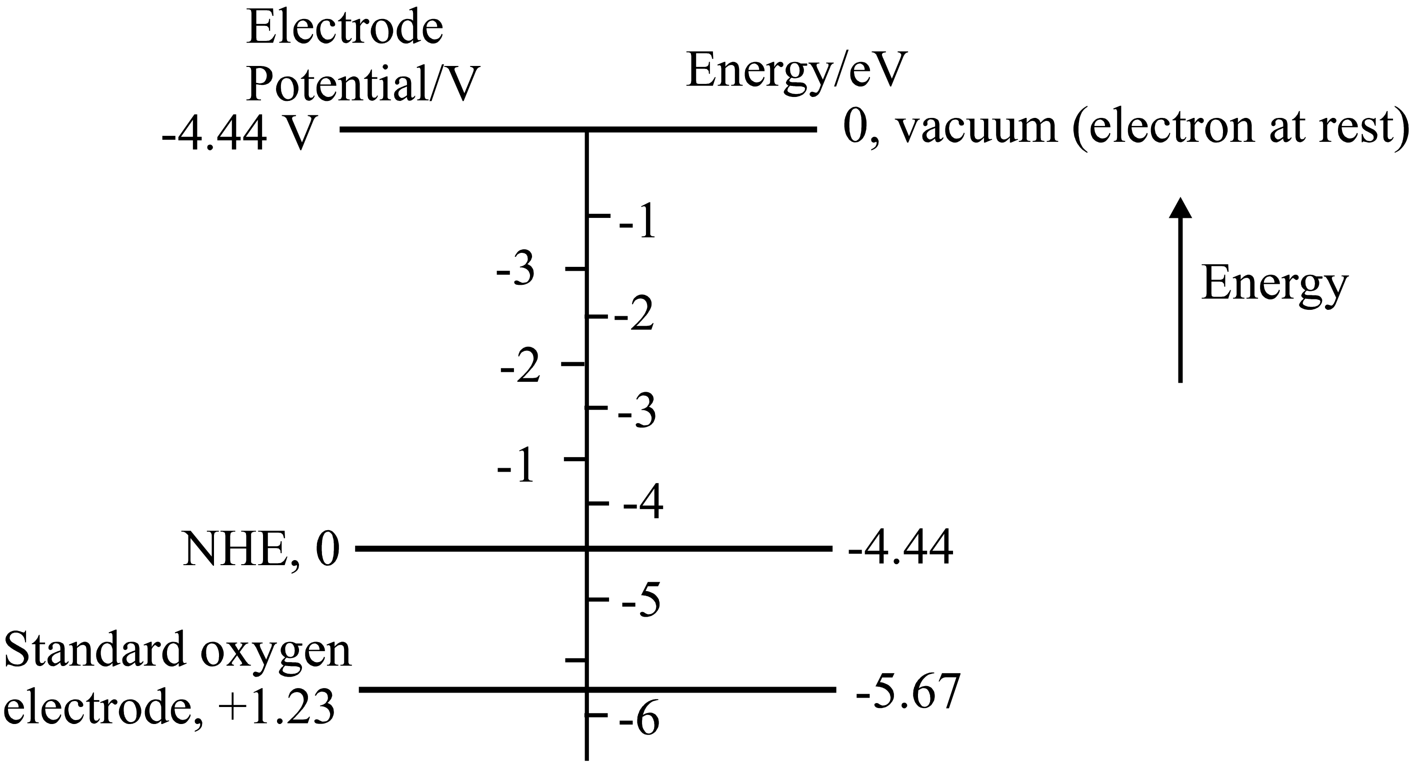
E(Ag/AgCl, sat.KCl) = E(NHE) – 0.196

E(Hg/HgO 1M KOH) = E(NHE) – 0.1100 + 0.05946pH

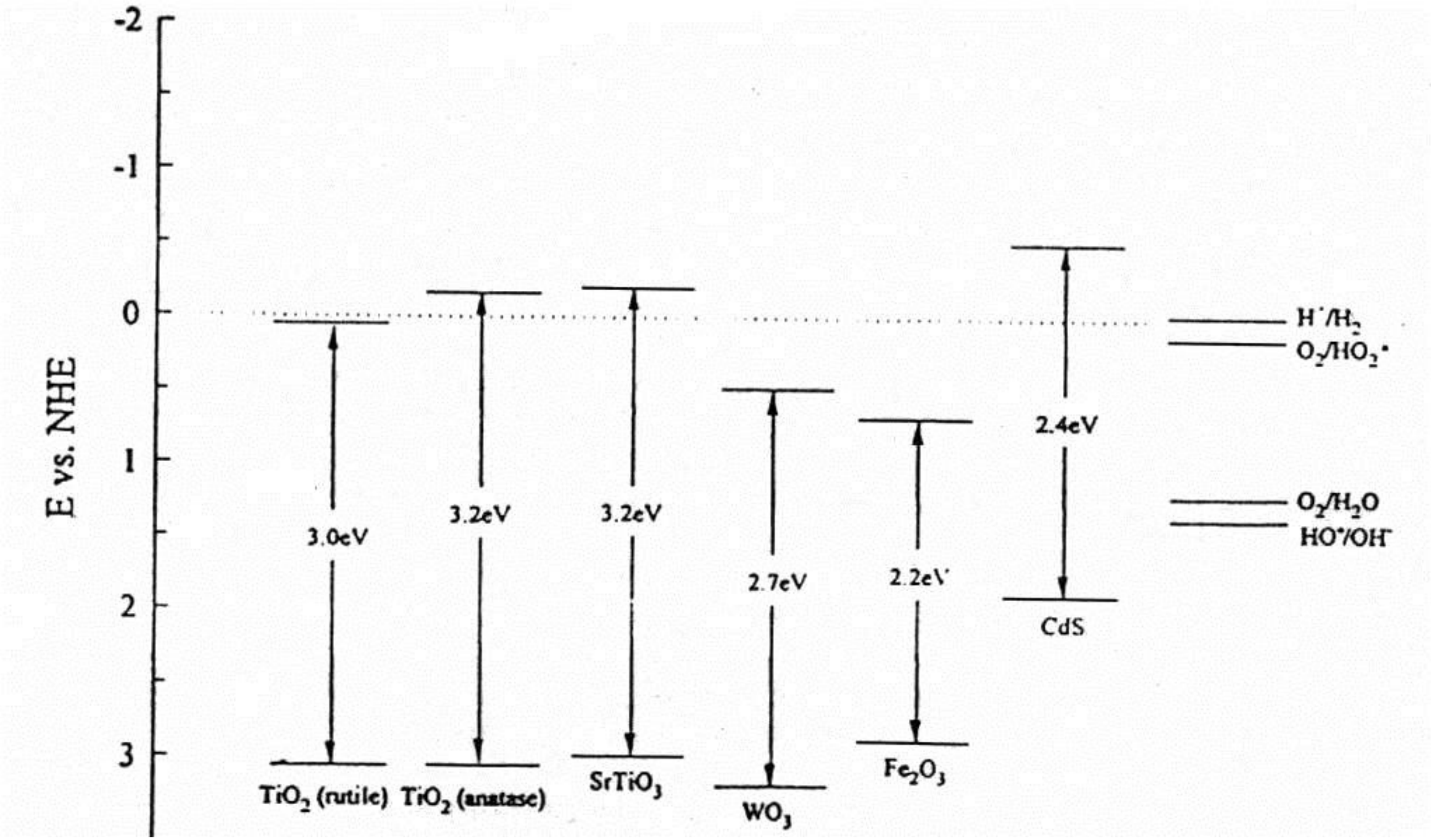
E(Hg/Hg_2SO_4) = E(NHE) – 0.6152



Potential vs. energy (vs. vacuum)



Example: Potential vs. energy (vs. vacuum)



3. 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

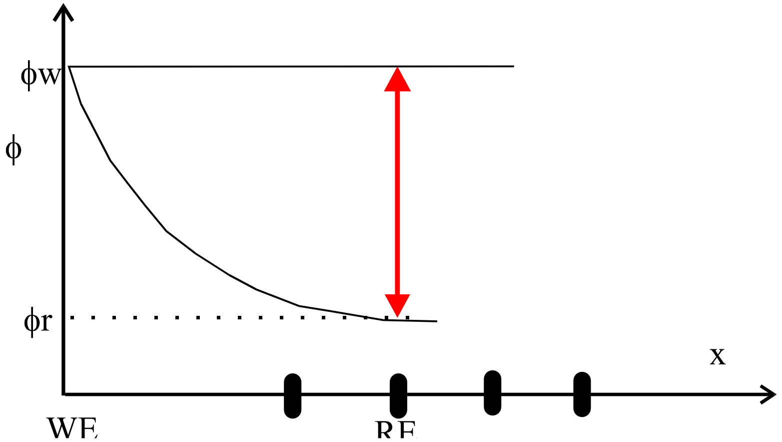
Overvoltage (η): the voltage shift caused by each kind of polarization

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

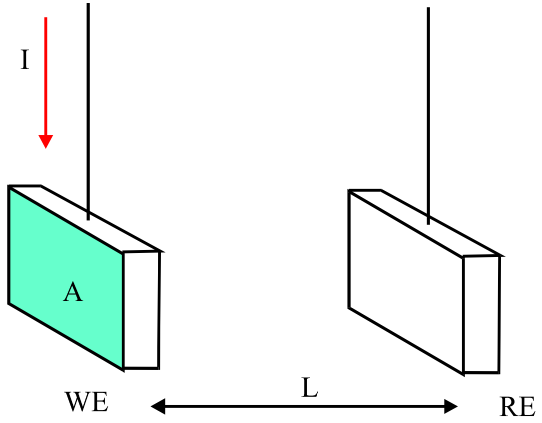
$$\mathbf{E = E_n + \eta_{ohm} + \eta_{act} + \eta_{conc}}$$

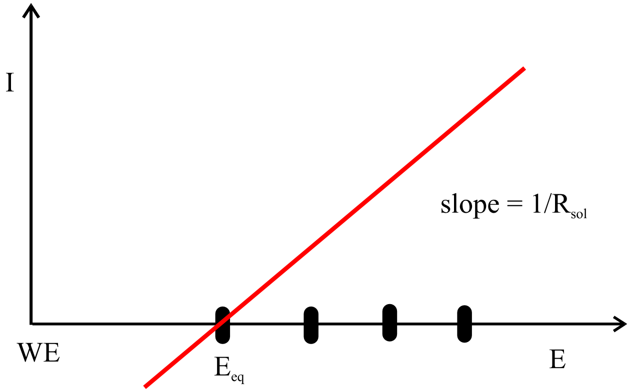
(i) **ohmic polarization**

$\eta_{ohm} = IR_{sol}$, "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) ↑→ η_{ohm} ↓ (by adding extra electrolyte: “supporting electrolyte”)

three-electrode system

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

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

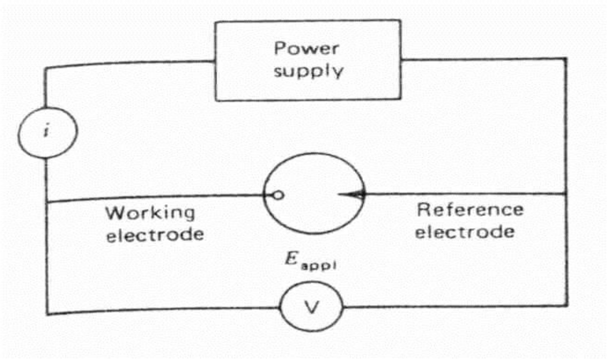
IR_s: ohmic drop in the solution (ohmic polarization) → should be minimized → short distance between working and reference electrode & three-electrode cell

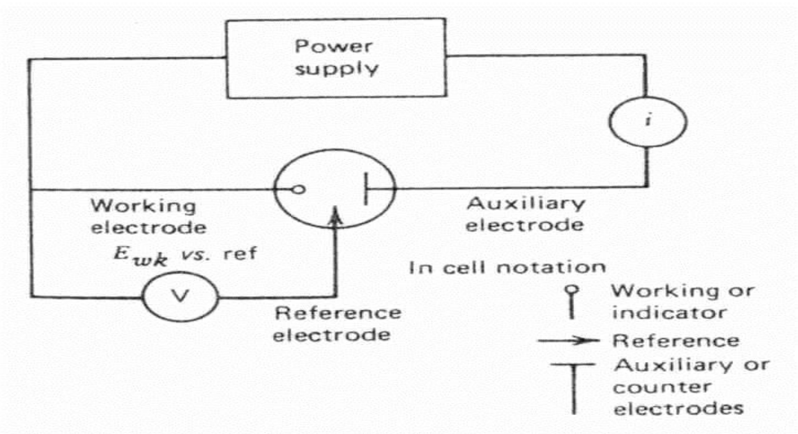
Two-electrode cell: iR_s problem due to high current flow

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





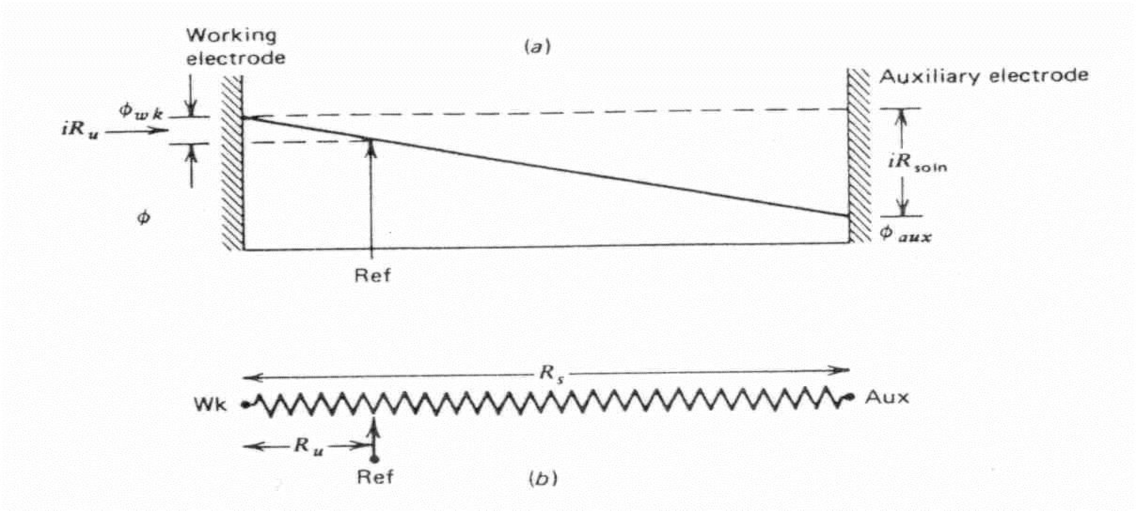


Figure) A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001.

(ii) **activation polarization**

slow electrode reaction → activation polarization; slow kinetics ∝ 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

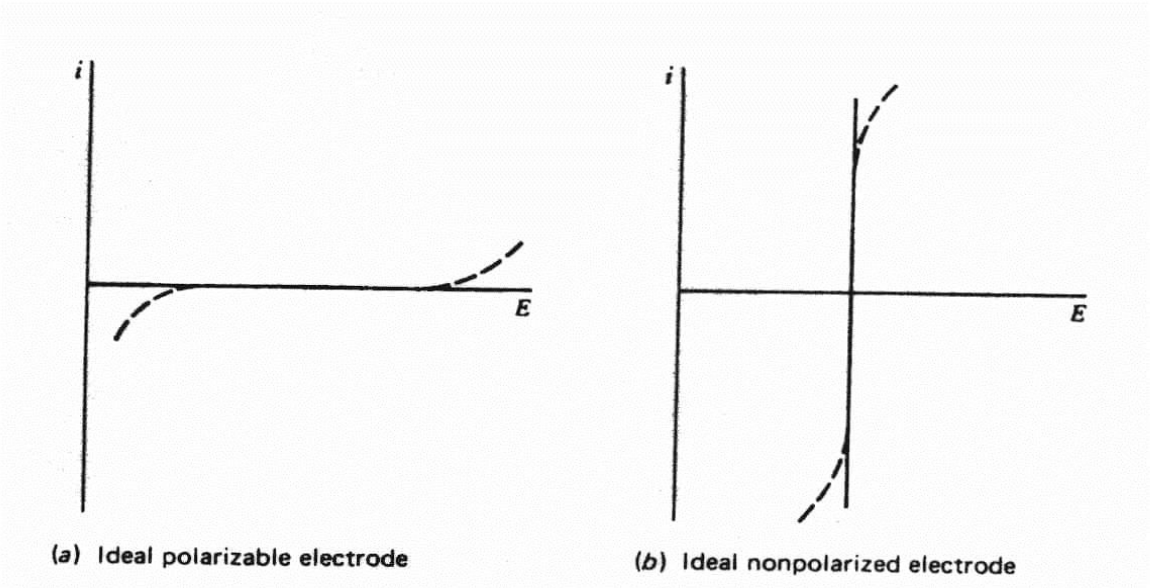
$$R \rightarrow O + ne^-$$

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

Limiting current

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

I–V Curves in Fuel Cell, Battery, Solar Cell