Introduction of Electrode Processes (Ch. 1)

Introduction

Electrochemical cells & reactions: thermodynamics and potentials

Nonfaradaic processes & electrode-solution interface

Capacitance and charge of an electrode
Electrical double layer

Faradaic processes & rates of electrode reactions

Reaction rates and current
Electrochemical cell resistance

Mass-transfer controlled reactions

Modes of mass transfer
Steady-state mass transfer
Non-steady-state mass transfer

Introduction

Electrochemistry: passage of electric current → chemical changes
chemical reactions → production of electric energy

Electrochemical cells & reactions

Electrode: junction between electronic conductor and ionic conductor (electrolyte) that the chemistry of electrochemistry occurs

e.g., solid metal, liquid metal, carbon, semiconductor

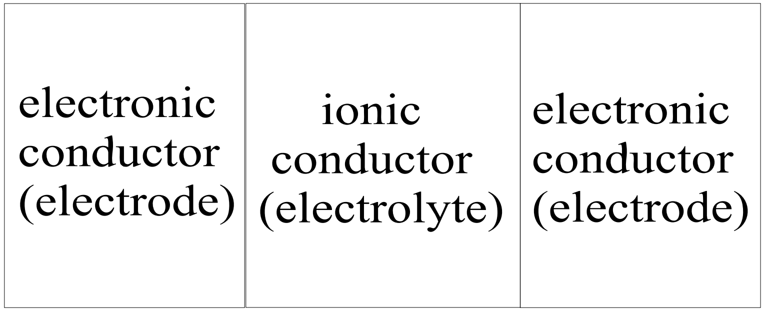
Electrolyte: substance that produces ions so enhance the electrical conductivity

e.g., liquid(aqueous, non-aq), gas(NH_3), solid electrolyte (polymer, ceramic)

Electrochemical cell: two electrodes + electrolyte

an ionic conductor sandwiched between two electronic conductors

e.g., aqueous solution of electrolyte between two pieces of metal, solid electrolyte between two metals



Cell potential (V, volts): 1 V = 1 J/C, energy to drive charge between electrodes

Electrochemical cell notation:

$Zn/Zn^{2+}, Cl^{-}/AgCl/Ag$ $\qquad$ $Pt/H_2/H^{+}, Cl^{-}/AgCl/Ag$

slash(/): phase boundary,

comma(,): two components in the same phase

double slash(//): phase boundary with negligible phase boundary

Two half-reactions

(i) interest in two equal electrodes (e.g., battery)

(ii) interest in **one electrode** only

- Working (or indicator) 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: $Pt/H_2(a=1)/H^+(a=1, \text{aqueous})$

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

- SCE (saturated calomel electrode): $Hg/Hg_2Cl_2/KCl(sat)$

$$Hg_2Cl_2(s) + 2e^- = 2Hg + Cl^- \quad E_{ref} = 0.242\ V \text{ vs. NHE}$$

- Ag/AgCl (silver-silver chloride): Ag/AgCl/KCl(sat or OO M)

$$AgCl(s) + e^- = Ag(s) + Cl^-(aq) \quad E_{ref} = 0.197\ V \text{ with saturated KCl}$$

Potentials of reference electrodes

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

E(SCE) = E(NHE) – 0.242

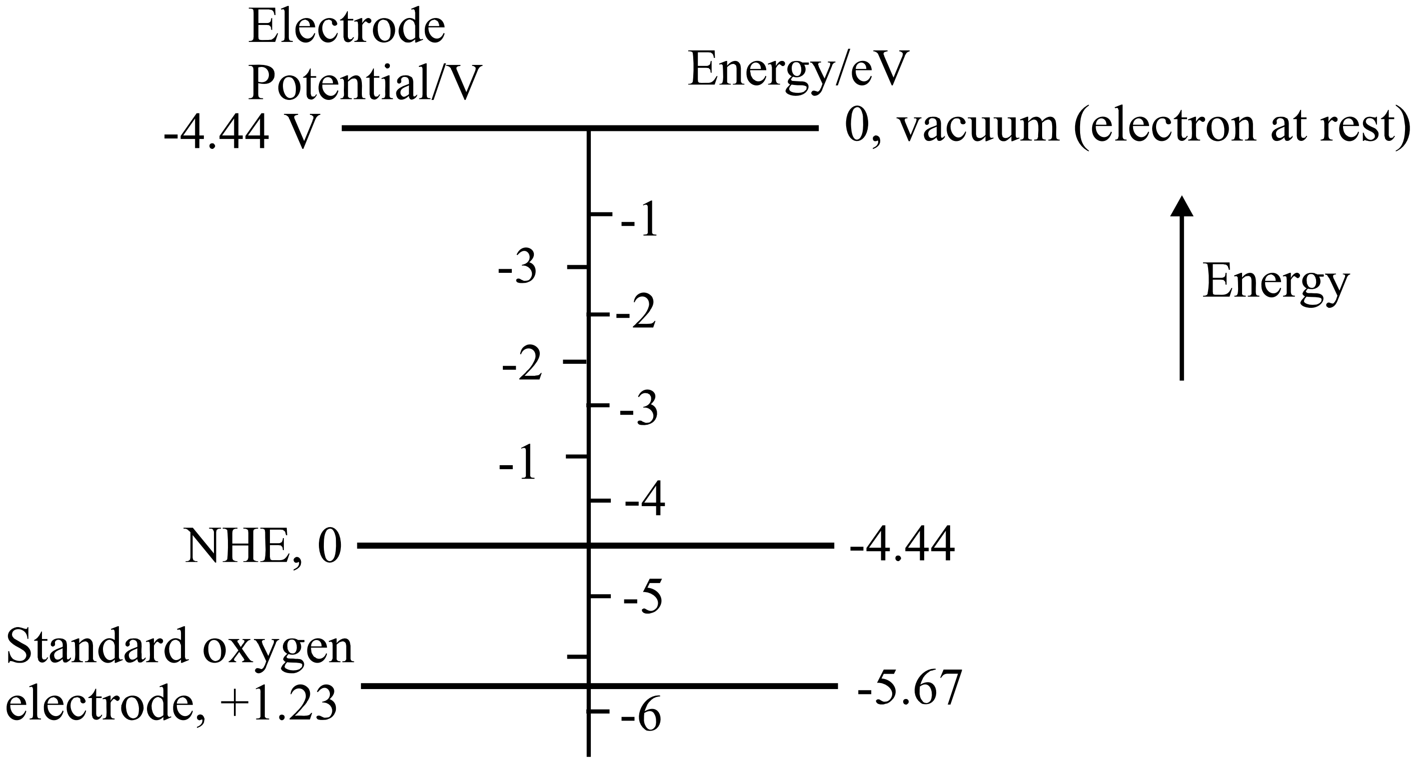
E(Ag/AgCl) = E(NHE) – 0.2223

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)



Electrode Potential/V

Energy/eV

-4.44 V

0, vacuum (electron at rest)

-1

-3

-2

-2

-3

-1

-4

NHE, 0

-4.44

-5

Standard oxygen electrode, +1.23

-5.67

-6

Energy

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 (reduction current)

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

Standard potential (E^0): critical potential at which these processes occur for the specific chemical substances in the system (p. 808, standard potential)

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

Electrochemical experiment:

- Electrochemical cell (WE/electrolyte/RE) + power supply
- Faraday's law: charge(Q, C(1 C = 6.24 x 10^{18} e^-) vs. extent of chemical reaction

"the passage of 96485.4 C causes 1 equivalent of reaction (e.g., consumption of 1 mole of reactant or production of 1 mole of product in a one-electron rxn)"

$$F = N_A Q_e = (6.02 \times 10^{23}\ \mathrm{mol^{-1}})(1.6022 \times 10^{-19}\ \mathrm{C}) = 96485\ \mathrm{Cmol^{-1}}$$

- Current (i): rate of flow of coulombs (or electrons) (1 A = 1 C/s)

current-potential (i vs. E) curve

open-circuit potential (zero-current potential or rest potential): potential measured by a high impedance voltameter. Since no current flows, it makes no difference if the circuit is interrupted, as by opening the switch

(i) redox couple (equilibrium established, e.g., Fig. 1.1.1): calculation of open-circuit potential is possible from the standard potentials of the half-reactions via the Nernst equation (open-circuit potential = equilibrium potential)

(ii) Overall equilibrium can not be established

e.g., Pt/H^+, Br^-/AgBr/Ag

Ag/AgBr electrode: AgBr + e = Ag + Br^-, 0.07 V

Pt/H^+, Br^-: not at equilibrium

→ equilibrium potential does not exist

OCV is not available from calculation

Then, open-circuit potential for this case? i-E curve?

1st electrode rxn: $2H^+ + e \rightarrow H_2$, -0.07 V vs. Ag/AgBr

2nd electrode rxn: oxidation of Br^- to Br_2

$Br_2 + 2e = 2Br^-$, 1.09 V vs. NHE (= 1.02 V vs. Ag/AgBr)

- Background limits (+1.02 V to +0.07 V)
- OCV: somewhere in background limits

(experimentally found, depends on impurities) e.g., Hg/H^+, $Br^-/AgBr/Ag$

OCV is not available from calculation

$2H^+ + e \rightarrow H_2$, 0.0 V vs. NHE (thermodynamic), slow rate: much more negative E ("overpotential")

oxidation of Hg to Hg_2Br_2 at 0.14 V

- Background limits (-0.9 V to +0.0 V): depends on electrode material & solution e.g., Hg/H^+, Br^-, Cd^{2+}(10^{-3} M)/AgBr/Ag

$Cd^{2+} + 2e = Cd(Hg)$ -0.4 V vs. NHE

- 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)

Faradaic and nonfaradaic 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 (0 to 0.8 V in Fig.1.1.5). 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

Ideal polarized electrode (ideal polarizable electrode) (IPE): no charge transfer over limited potential ranges

e.g., Hg in KCl (+0.25 V to -2.1 V), alkane thiol on Au

Capacitance and charge of an electrode

- IPE 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 μ F capacitor

→ current will flow until 20 μ C accumulated

Electrode-solution interface: $q^M = -q^S$ “electrical double layer”

q^M: very thin layer (<0.1 Å), charge density (μ C/cm^2) $\sigma^M = q^M/A$

Typical double-layer capacitance (C_d): 10 ~ 40 μ F/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)

Double layer capacitance & charging current

IPE and ideal reversible electrode

e.g.,) Hg/K$^+$, Cl-/SCE, Hg: ideal polarized electrode

C_{SCE}, C_d: capacitances of SCE and double layer, R_s: solution resistor

$C_T = C_{SCE}C_d/(C_{SCE} + C_d)$, $C_{SCE} >> C_d \rightarrow C_T \approx C_d \rightarrow$ RC circuit

- Consider several common electrical perturbations

(a) Voltage (or potential) step:

potential step: E, E_C of capacitor, E_R of resistor

$$q = C_d E_C$$

$$E = E_R + E_C = iR_s + q/C_d$$

$$i = dq/dt$$

$$dq/dt = -q/(R_s C_d) + E/R_s$$

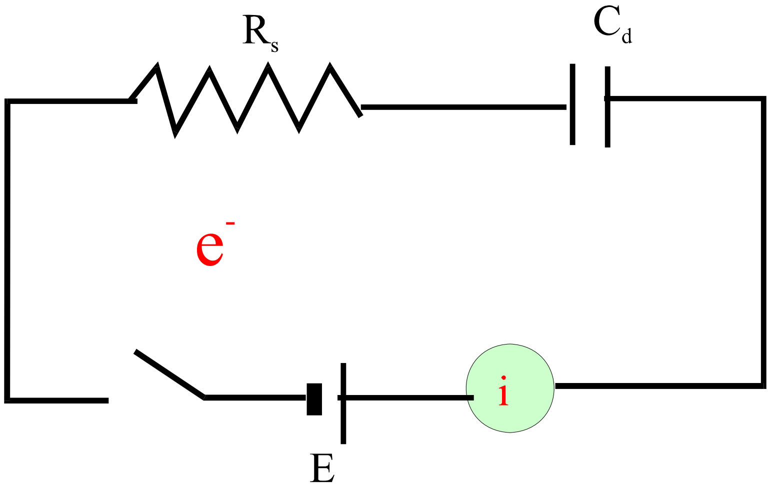
$$q = 0 \text{ at } t = 0 \rightarrow q = EC_d[1 - \exp(-t/R_s C_d)]$$

By differentiating,

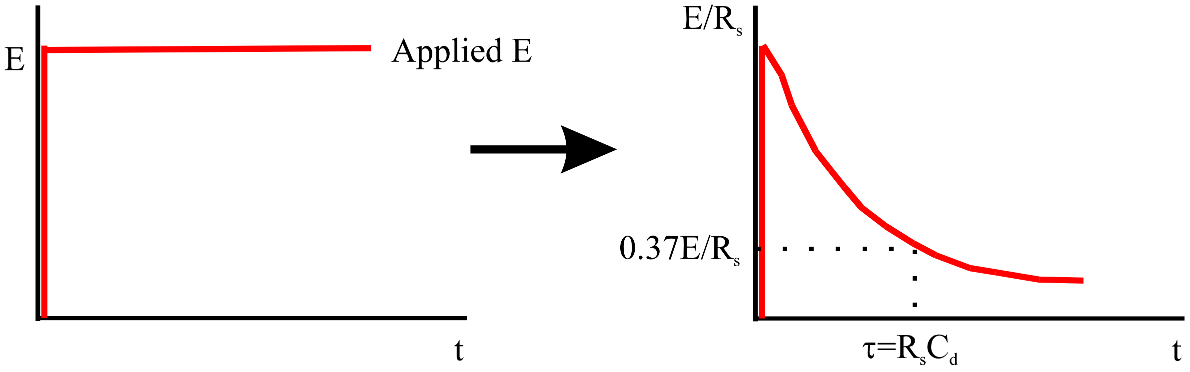
$$I = (E/R_s)\exp(-t/R_s C_d)$$

At time constant $\tau = R_s C_d$ → current for charging the double layer capacitance drops to

$$37\ \% \text{ at } \tau = t,\ 5\ \% \text{ at } \tau = 3t$$



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



(b) Current step

$E = E_R + E_C = iR_s + q/C_d$
$q = \int idt$ and i is constant

$$E = iR_s + (i/C_d)\int dt$$
$$E = i(R_s + t/C_d)$$

- Potential increases linearly with time

(c) Potential sweep

Linear potential sweep with a sweep rate v (in V/s)

$$E = vt$$

$E = E_R + E_C = iR_s + q/C_d$

$$vt = R_s(dq/dt) + q/C_d$$

If $q = 0$ at $t = 0$, $i = vC_d[1 - \exp(-t/R_sC_d)]$

- Current rises from 0 and attains a steady-state value (vC_d): measure C_d

- Cyclic linear potential sweep

Faradaic processes & rates of electrode reactions

Electrochemical cells (faradaic current are flowing): types and definitions

(i) Galvanic cell: reactions occur spontaneously at the electrodes when they are connected externally by a conductor. Converting chemical energy into electrical energy. e.g., primary battery, secondary battery (discharging (방전)), fuel cell

(ii) Electrolytic cell: reactions are effected by an external voltage. Electrical energy to chemical reactions. e.g., electrolytic syntheses, electrorefining (e.g., copper), electroplating, secondary battery (charging(충전시))

electrons produced: **oxidation**, “**anode**”
electrons consumed; **reduction**, “**cathode**”
In galvanic cell, anode is negative with respect to the cathode
In electrolytic cell, cathode is negative with respect to the anode

The electrochemical experiment & variables in electrochemical cells

The electrochemical experiment

Current *vs.* reaction rate

$$i\ (A) = dQ/dt\ (C/s)$$

$$Q/nF = N\ (mol)$$

n: # of electrons in reaction (2 for reduction of Cd^{2+})

$$Rate\ (mol/s) = dN/dt = i/nF$$

Electrode process: heterogeneous reaction

$$Rate\ (mol s^{-1} cm^{-2}) = i/nFA = j/nF$$

j: current density (A/cm^2)

Electrode reaction: i-E curves

Polarization: departure of the cell potential from the equilibrium potential

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

Ideal polarizable electrode: a very large change in potential upon small current

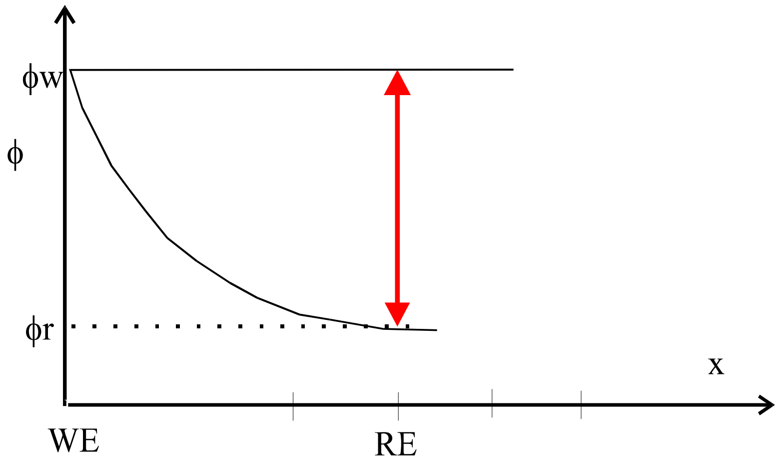
Ideal nonpolarizable electrode: potential does not change upon passage of current (e.g., reference electrode)

Factors affecting electrode reaction rate and current

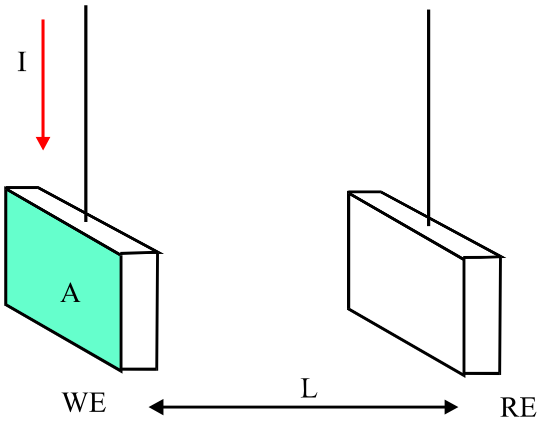
1. Mass transfer
2. Electron transfer at the electrode surface
3. Chemical reactions
4. Other surface reactions: adsorption, desorption, electrodeposition

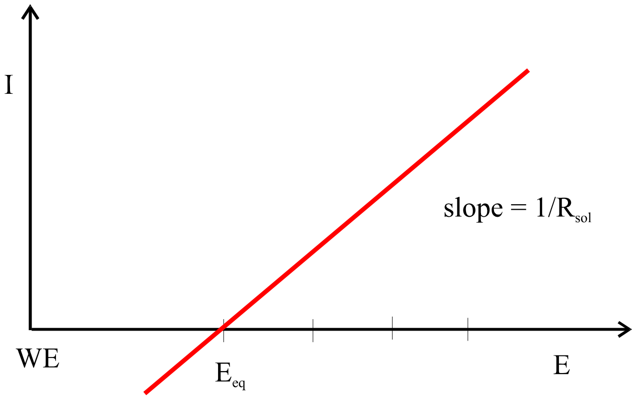
Electrochemical cells & cell resistances

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



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





If free of charge transfer and mass transfer overpotentials, slope = $1/R_{sol}$

Electrochemistry needs to minimize η_{ohm}
κ (conductivity) ↑→ η_{ohm} ↓ (by adding extra electrolyte: “supporting electrolyte”)
Closer between WE and RE
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**

Mass transport-controlled reactions

Modes of mass transfer

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

Mass transfer-controlled reaction

$$v_{rxn} = v_{mt} = i/nFA$$

Modes 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)

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

Where $J_i(x)$; the flux of species i ($mol\,sec^{-1}cm^{-2}$) 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)

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 (excess supporting electrolyte),

$$O + ne^- = R$$

The rate of mass transfer,

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

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

$$v_{mt} = m_O[C_O^b - C_O^s]$$

where C_O^b is the concentration of O in the bulk solution, C_O^s is the concentration at the electrod surface

m_O is “mass transfer coefficient (cm/s)” ($m_O = D_O/\delta$)

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

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

largest rate of mass transfer of O when $C_O^s = 0 \rightarrow$ "limiting current"

$$\mathbf{i_{l,c} = nFAm_O C_O^b}$$

Maximum rate when limiting current flows

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

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

C_O^s varies from C_O^b at i = 0 to negligible value at $i = i_l$

If kinetics of electron transfer are rapid, the concentrations of O and R at the electrode surface are at equilibrium with the electrode potential, as governed by the Nernst equation for the half-reaction

$$\mathbf{E = E^{0\,\prime} + (RT/nF)\ln(C_O^s/C_R^s)}$$

$E^{0\prime}$: formal potential (activity coeff.), cf. E^0 (standard potential)

(a) R initially absent

When $C_R^b = 0$, $\quad C_R^s = i/nFAm_R$

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

$$\mathbf{E = E^{0\prime} - (RT/nF)\ln(m_O/m_R) + (RT/nF)\ln(i_{l,c} – i/i)}$$

i-E plot

When $i = i_{l,c}/2$, $E = E_{1/2} = E^{0\prime} - (RT/nF)\ln(m_O/m_R)$

$E_{1/2}$ is <u>independent of concentration & characteristic of O/R system</u>

$$E = E_{1/2} + (RT/nF)\ln(i_{l,c} – i/i)$$

Plot of E vs. $\log(i_{l,c} – i/i)$: straight, slope = 2.3RT/nF (or 59.1/n mV^{-1} at 25ºC)

E intercept = $E_{1/2}$ (when $m_O \sim m_R \rightarrow E_{1/2} \sim E^{0\prime}$)

(b) Both O and R initially present

Same method,

$$C_R^s/C_R^b = 1 – (i/i_{l,a})$$

$$i_{l,a} = -nFAm_RC_R^b$$

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

Put these equations to $E = E^{0\,\prime} + (RT/nF)\ln(C_O^s/C_R^s)$

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

When $i = 0$, $E = E_{eq}$ and the system is at equilibrium

Deviation from E_{eq}: concentration overpotential

(c) R insoluble

Suppose R is a metal (plating),

$a_R = 1$, $E = E^{0\prime} + (RT/nF)\ln C_O{}^s$

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

$$\mathbf{E = E^{0\prime} + (RT/nF)\ln C_0{}^b + (RT/nF)\ln[(i_l - i)/i_l]}$$

When $i = 0$, $E = E_{eq} = E^{0\prime} + (RT/nF)\ln C_O{}^b$

Deviation from E_{eq}: concentration overpotential

$$\eta_{conc} = E - E_{eq} = (RT/nF)\ln[(i_l - i)/i_l]$$

When $I = i_l$, $\eta_{conc} \rightarrow \infty$ (complete concentration polarization)

$$1 - i/i_l = \exp(nF\,\eta_{conc}/RT)$$

$e^x = 1 + x + \ldots = 1 + x$ (when x is small)

At small deviation of potentials from E_{eq}, i- η_{conc} is linear

$$\eta_{conc} = -RTi/nFi_l$$

Mass transfer resistance, $R_{mt} = RT/nF|i_l|$

Non-steady state mass transport: diffusion control

Time-dependent (transient) phenomena

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)

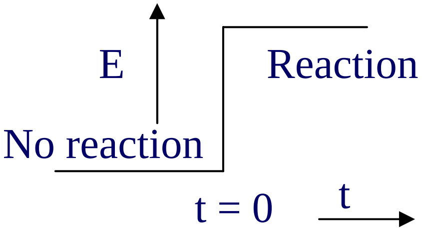
The variation of concentration with time due to diffusion → Fick's second law

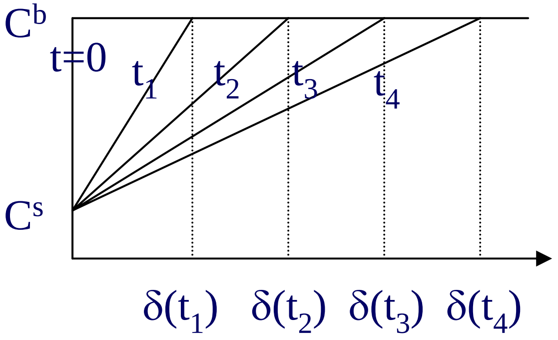
$$\partial C/\partial t = -D(\partial^2 C/\partial x^2) \qquad \text{1-D}$$

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

$$v_{mt} = D(\partial C/\partial x) = D_O(C_O^b - C_O^s)/\delta(t) = i/nFA$$

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,

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

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

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

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

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

In the absence of convection: current continues to decay
In a convection system: approaches to steady-state value