

전기화학 반응 기본 개념 원리

Basic Principles in Electrochemistry

Uk Sim

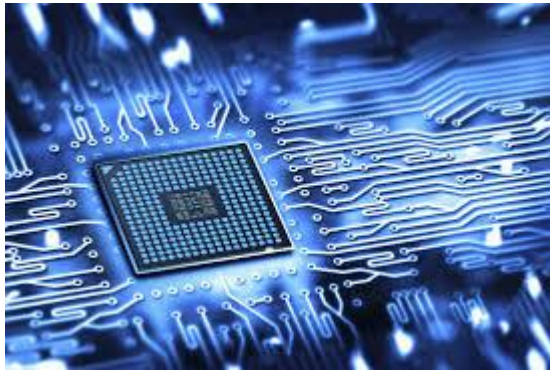
Department of Materials Science & Engineering

Chonnam National University

Electrochemistry

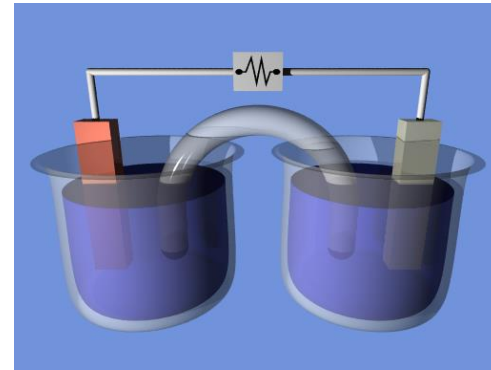
Interrelation of electrical and chemical effects !

**Electronic
Field**



**Electric
current**

**Chemical
Field**



**Electric/ Ionic current and
Chemical Reaction**

Electrochemical Reactions



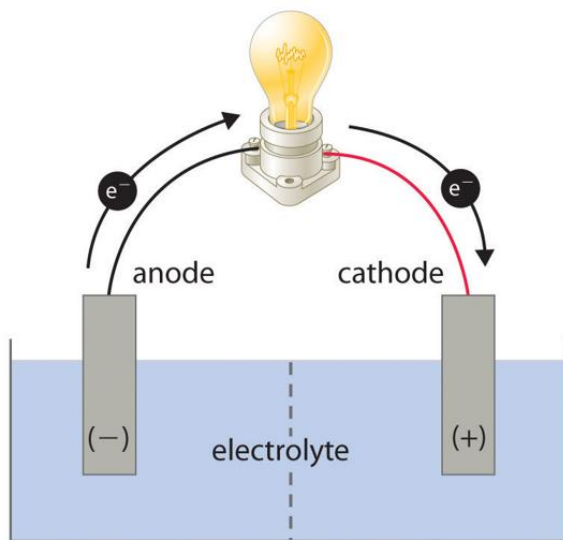
Electrochemical Reduction

Electrochemical Oxidation

Cathode

Anode

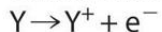
Two Systems of Electrochemistry



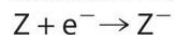
GALVANIC CELL

Energy released by spontaneous redox reaction is converted to electrical energy.

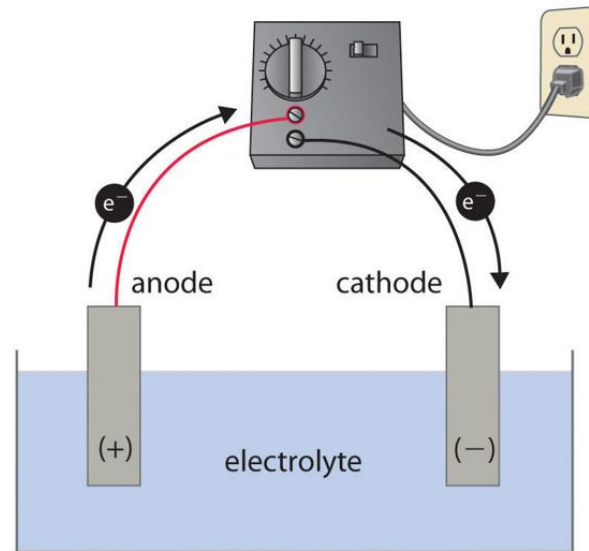
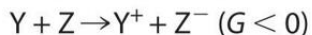
Oxidation half-reaction:



Reduction half-reaction:



Overall cell reaction:



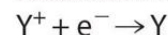
ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

Oxidation half-reaction:



Reduction half-reaction:



Overall cell reaction:



Chemical Reaction

→ Electric current

Electric current

→ Chemical Reaction

Two-electrode and three-electrode cells

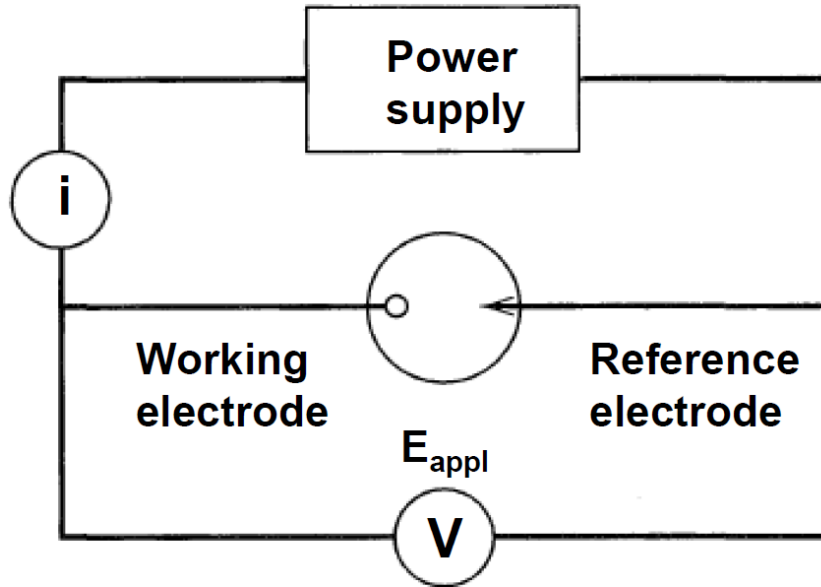


Figure 1.3.9 Two-electrode cell.

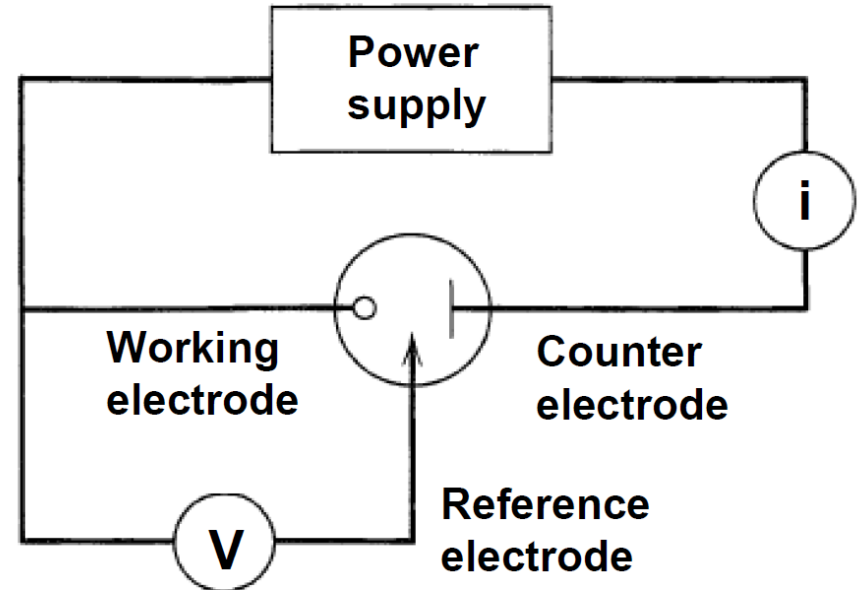


Figure 1.3.10 Three-electrode cell and notation for the different electrodes.

- Real electrochemical system consists of cathode and anode
- Under conditions when iR_s is small (say less than 1-2 mV), this two-electrode cell can be used to determine the i - E curve
- However, it is hard to know the exact amount of current if iR_s is high
 → 3 electrode system is necessary
- Current is passed between the WE and CE
- Potential of the WE is monitored relative to a separate RE
- A negligible current is drawn through R_E due to the high impedance of voltmeter.
- Used in most electrochemical experiments.

Reference Electrodes

- There are experimental reasons for the choice of a reference electrode.

Ag/AgCl/KCl (saturated, aqueous)

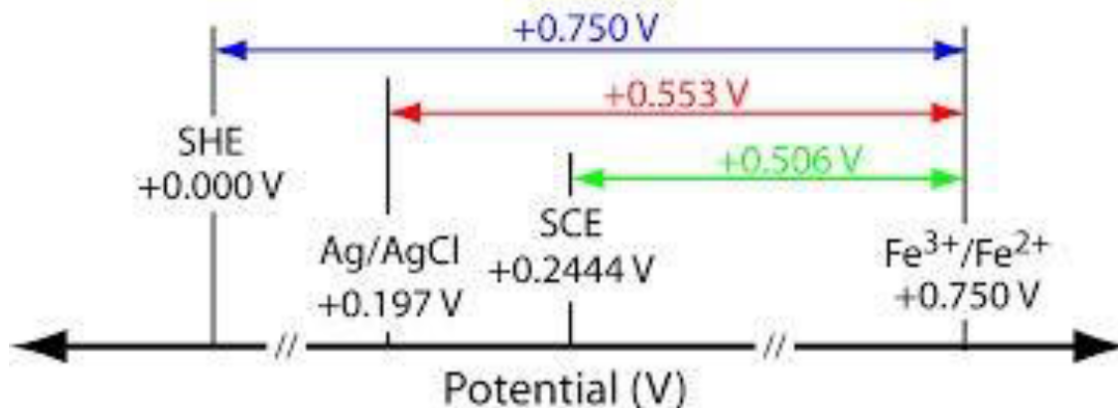
- Smaller temperature coefficient of potential than an SCE.
➔ It can be built more compactly.

Hg/Hg₂SO₄/K₂SO₄ (saturated, aqueous)

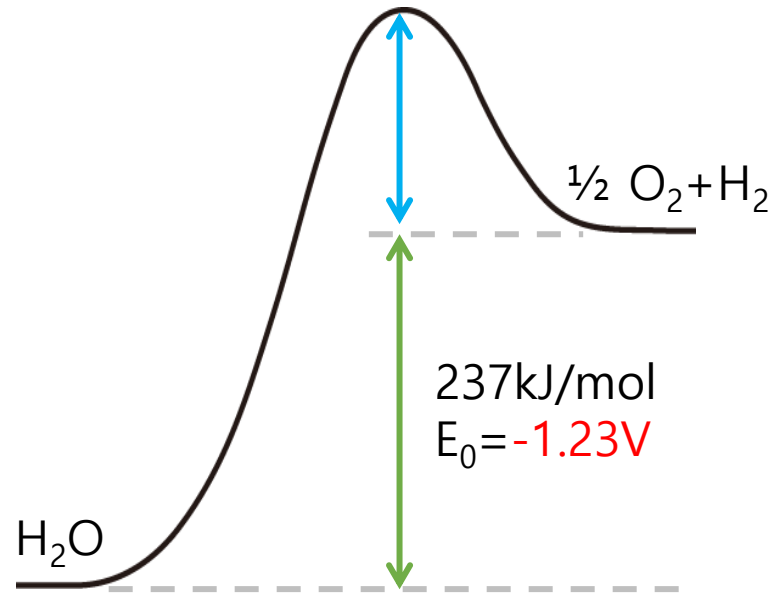
- When chloride is not acceptable, the mercurous sulfate electrode is used.

Ag/Ag⁺ (0.01 M in CH₃CN)

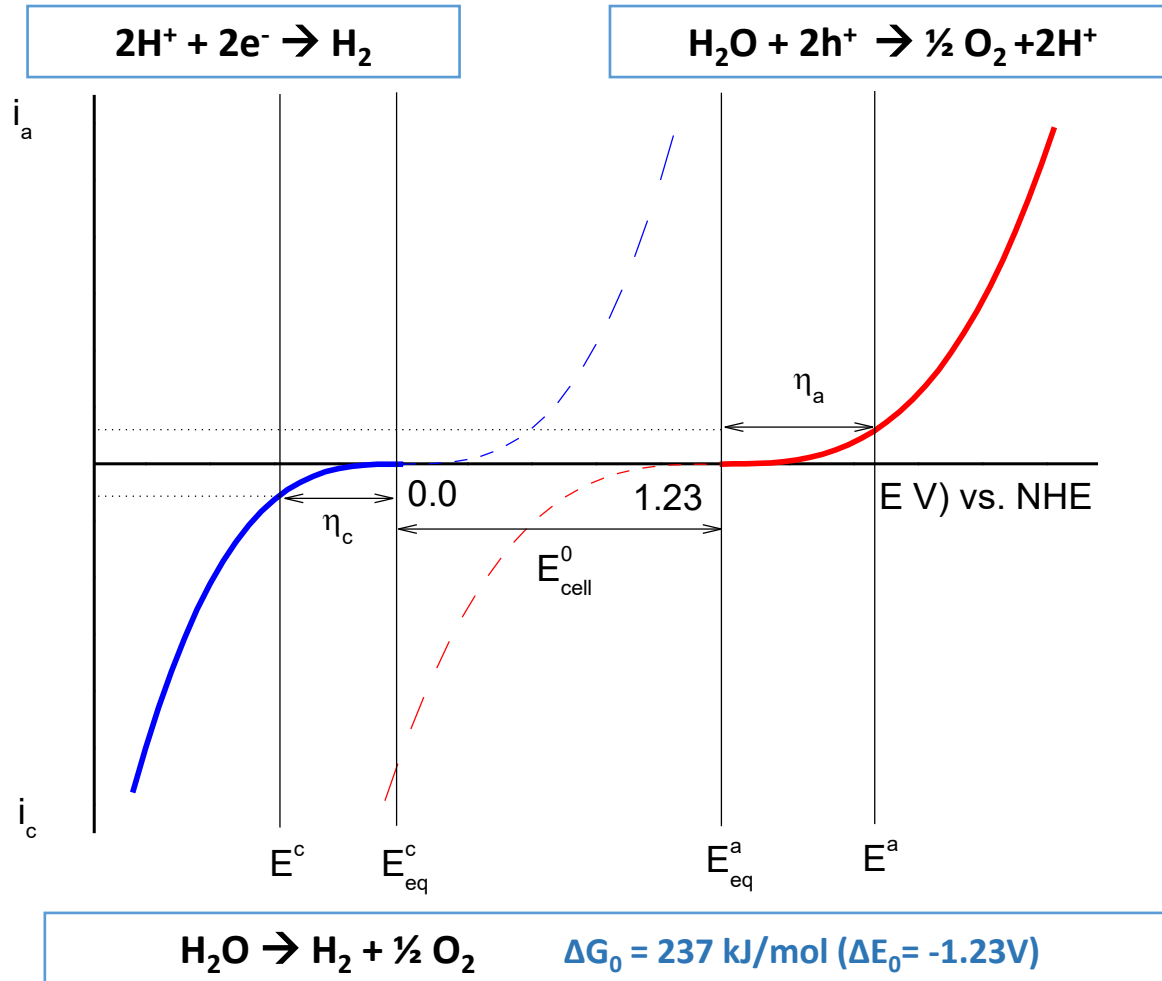
- With a nonaqueous solvent, Ag/Ag⁺ electrode is used to prevent leakage of water.



Overpotential for Water Splitting

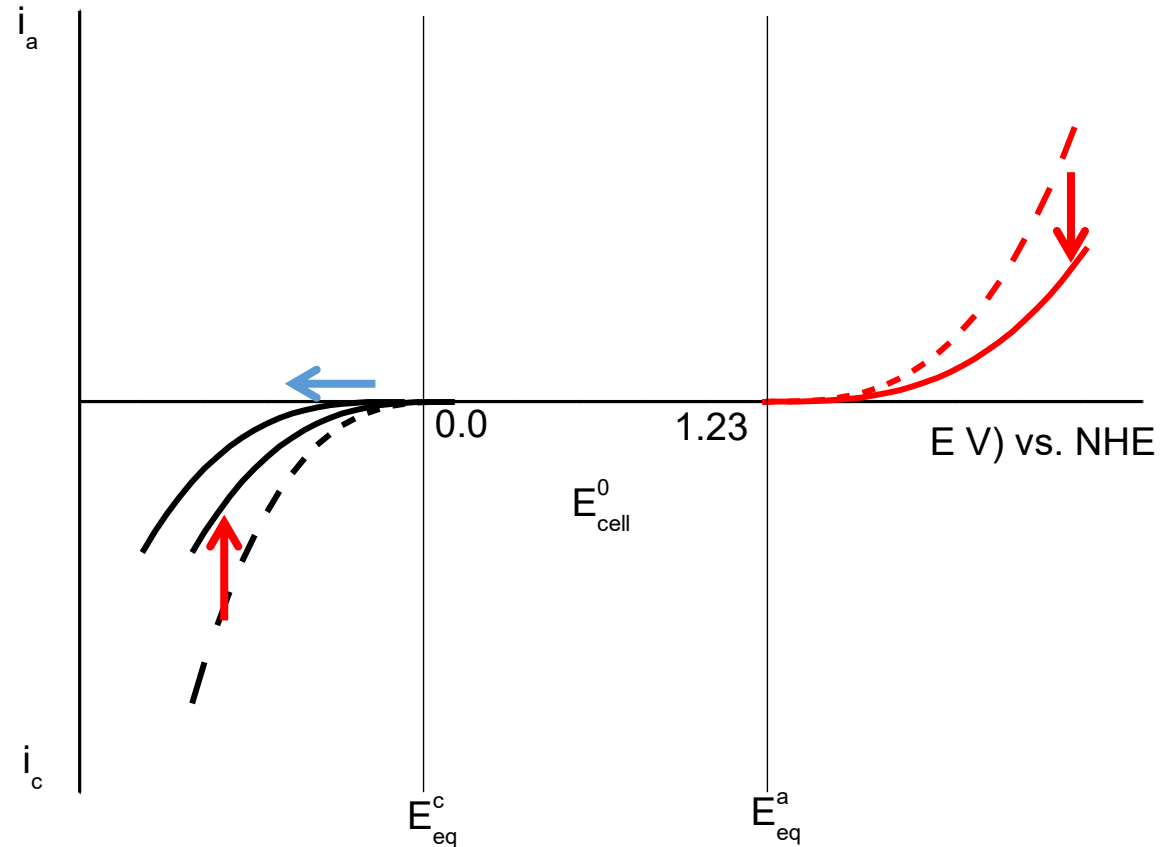


Potential for Electrolysis of Water



$$E_{\text{appl}} = E_{\text{cell}}^0 + \eta_c + \eta_a$$

Overpotential for Electrolysis of Water

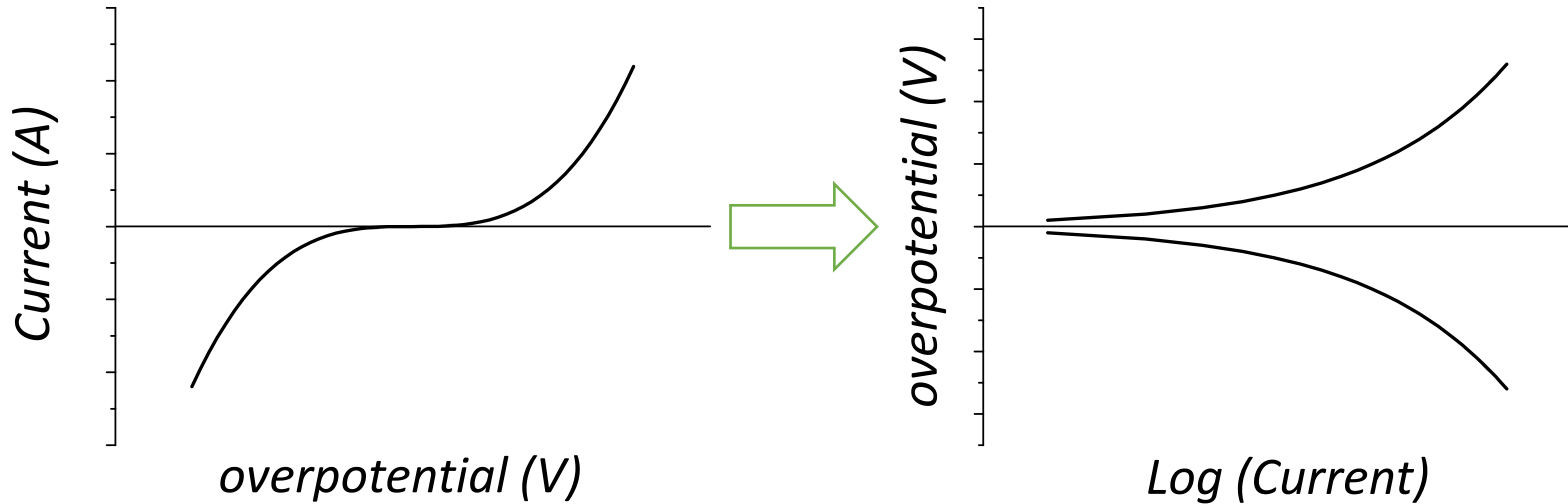


1. Onset Potential & Overpotential

2. Tafel slope

Tafel plot

“Tafel” : Swiss chemist **Julius Tafel** (1862-1918)



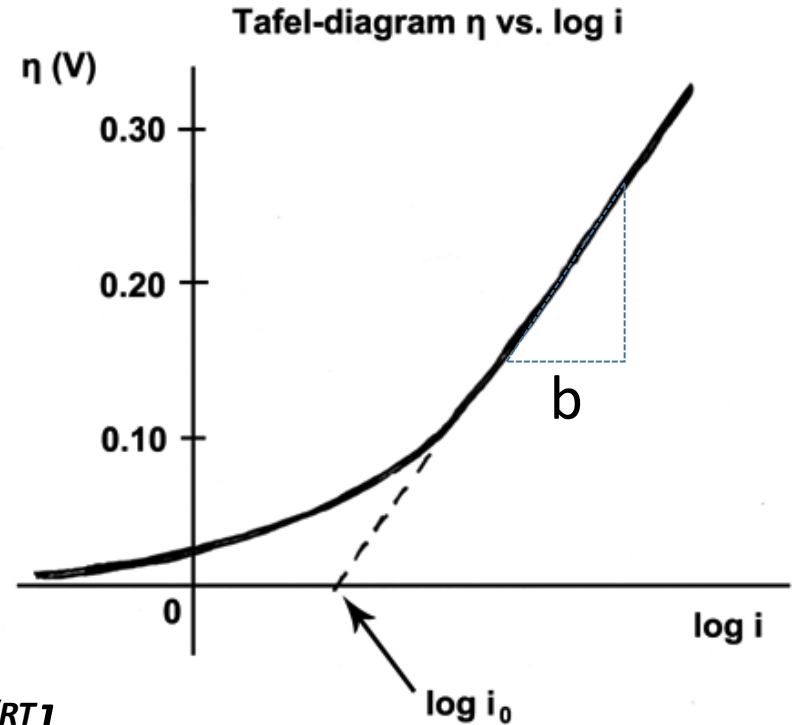
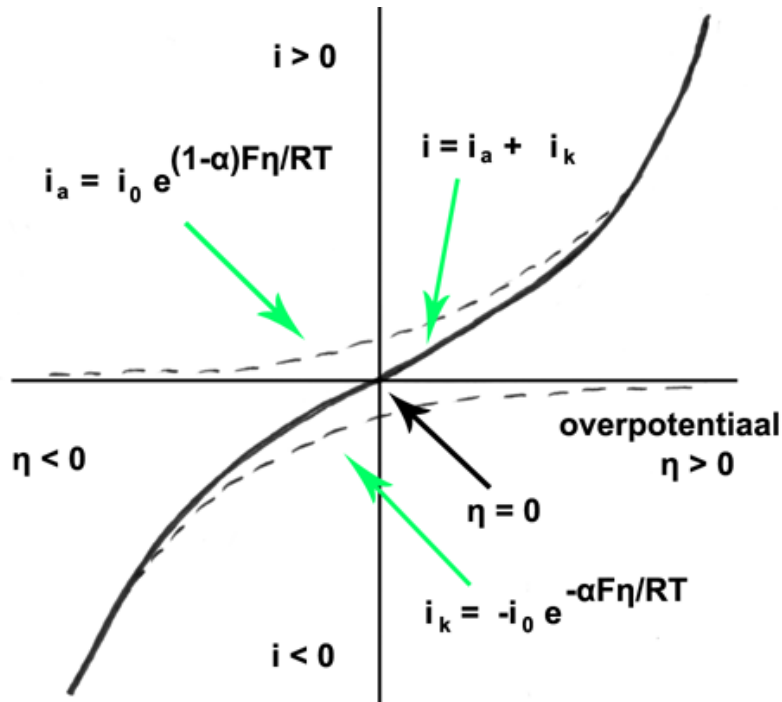
$$\eta = b \log \frac{I}{I_0}$$

η : overpotential

I : the observed current, I_0 : the exchange current

b : Tafel slope, a measure of the potential increase required to increase the resulting current 1 order of magnitude

Tafel plot



Butler-Volmer eqn: $i_{net} = i_0 [e^{-\alpha n F \eta / RT} - e^{(1-\alpha) n F \eta / RT}]$

if $\eta < (118/n) \text{ mV}$, $i = i_0 n F / RT (-\eta)$ ($\because e^x \approx 1+x$)

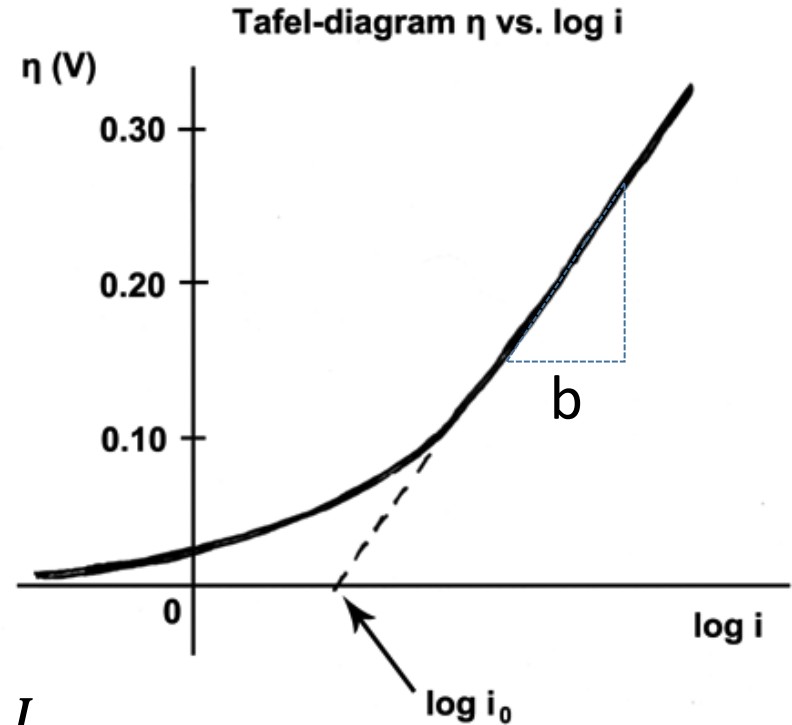
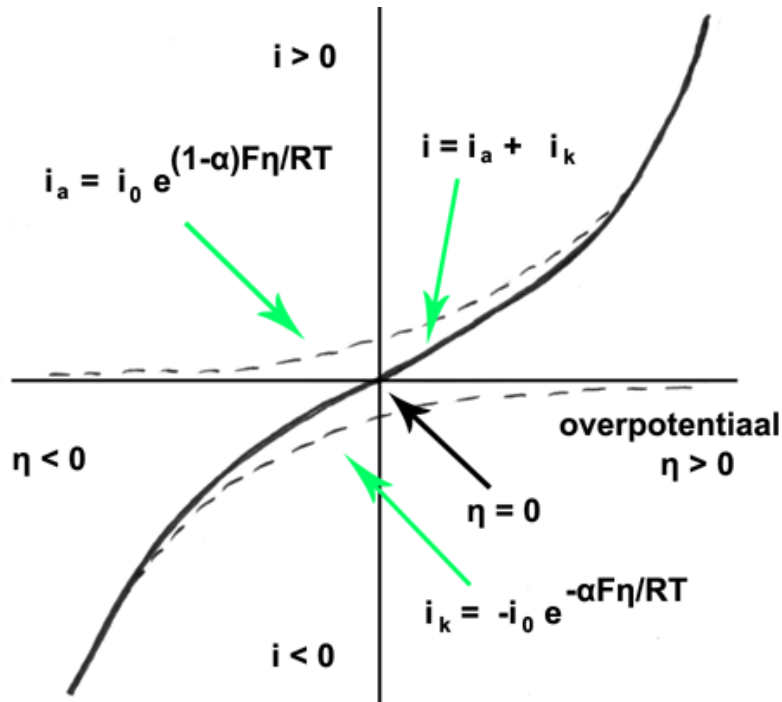
if $\eta \ll 0$, $i_{net} \approx i_c = i_0 e^{-\alpha n F \eta / RT} \rightarrow \log |i_{net}| = \log i_0 - \alpha n F \eta / 2.303 RT$

if $\eta \gg 0$, $i_{net} \approx i_a = i_0 e^{-(1-\alpha) n F \eta / RT} \rightarrow \log |i_{net}| = \log i_0 - (1-\alpha) n F \eta / 2.303 RT$

$\eta = b \log \frac{I}{I_0}$

$b = 2.303 RT / \alpha n F \eta$ or $2.303 RT / (1-\alpha) n F \eta$

Tafel plot



$$\eta = b \log \frac{I}{I_0}$$

I_0 : The exchange current. For Pt, $\log i_0$ (A/cm²) ≈ -3

b : Tafel slope, a measure of the potential increase required to increase the resulting current 1 order of magnitude. For Pt, $b \approx 30$ mV/decade

Tafel slope

- **Tafel slope**

- It is an inherent property of the catalyst determined by the rate-limiting step for HER.
- It is also related to the adsorbed hydrogen coverage (ϑ_{H}) on the surface of the electrode.

- **Hydrogen Evolution Reaction in acidic solution**



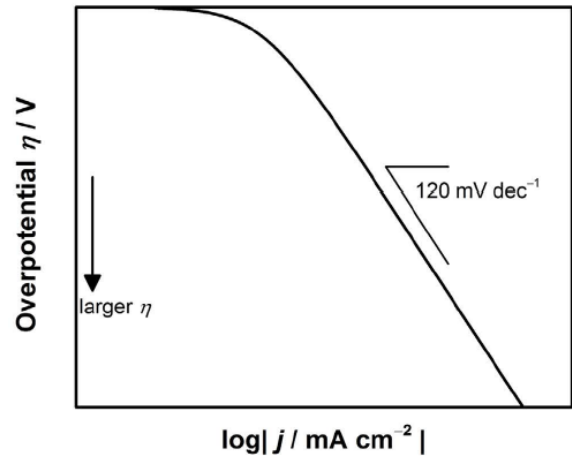
R : ideal gas constant,
 T : absolute temperature,
 α : symmetry coefficient ($\alpha \approx 0.5$)
 F : Faraday constant

- (1) Discharge step *(Volmer reaction)*
(2) Electrochemical desorption step *(Heyrovsky reaction)*
(3) Recombination step of adsorbed hydrogen *(Tafel reaction)*

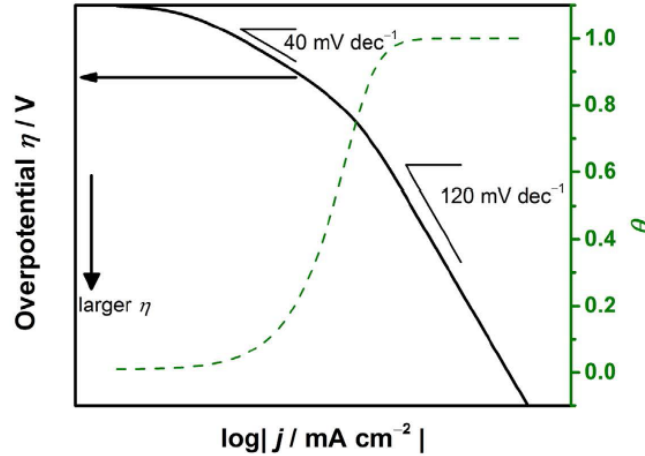
- *Rate determining step is,*

- *Heyrovsky reaction:* $\vartheta_{\text{H}} \approx 0 \sim 1 \rightarrow b = 40 \sim 118 \text{ mV/dec}$
- *Tafel reaction:* $\vartheta_{\text{H}} \approx 1 \rightarrow b = 30 \text{ mV/dec}$

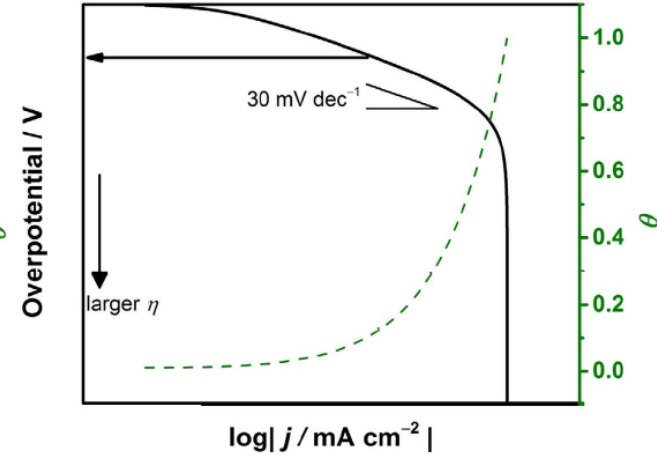
Tafel Slope and Hydrogen Evolution Reaction Mechanism



$$I = nFAk_6^0 a_{\text{H}_3\text{O}^+} \exp(-\alpha_6 f \eta_6).$$



$$I = nFA \frac{k_7^0 K_6^0 a_{\text{H}_3\text{O}^+}^2 \exp(-\alpha_7 f \eta_7)}{a_{\text{H}_2\text{O}} \exp(f \eta_6) + K_6^0 a_{\text{H}_3\text{O}^+}}.$$



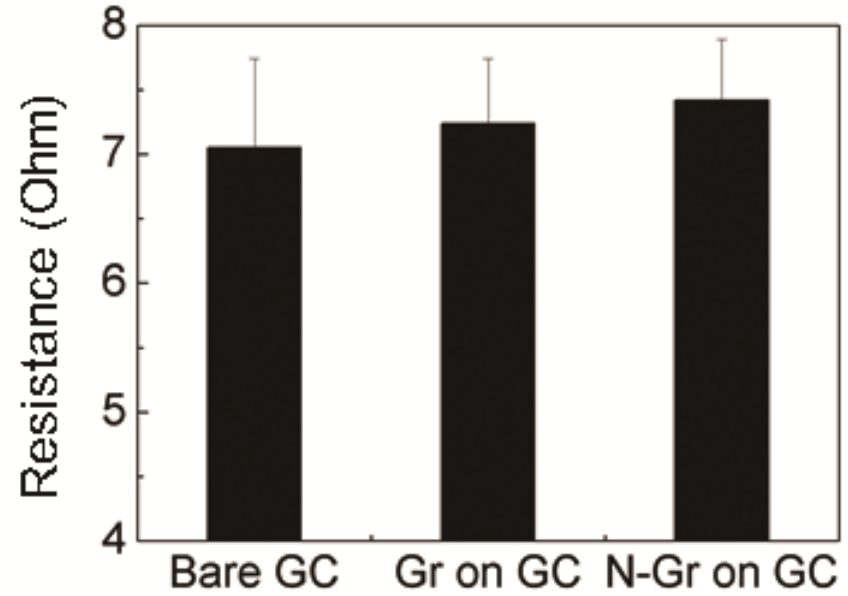
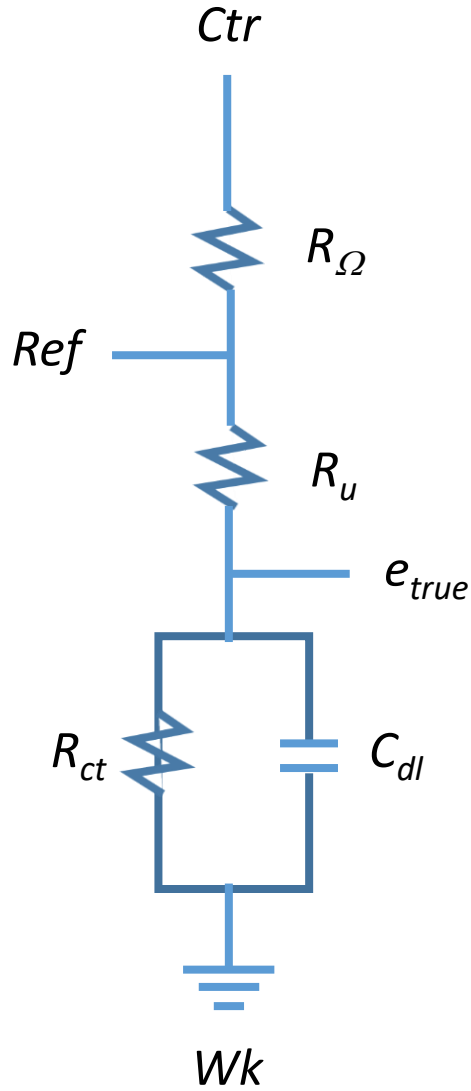
$$I = nFAk_8^0 \left[\frac{K_6^0 a_{\text{H}_3\text{O}^+}}{a_{\text{H}_2\text{O}} \exp(f \eta_6) + K_6^0 a_{\text{H}_3\text{O}^+}} \right]^2.$$



Tafel slope is potential and coverage dependent!

If overpotential of considered region is too small,
the Tafel analysis leads to misrepresentation of the rate-determining step

iR Compensation



$$e_{true} \text{ (vs. ref)} = | e_1 + e_2 + e_3 | - | iR_u |$$

R_u : uncompensated resistance

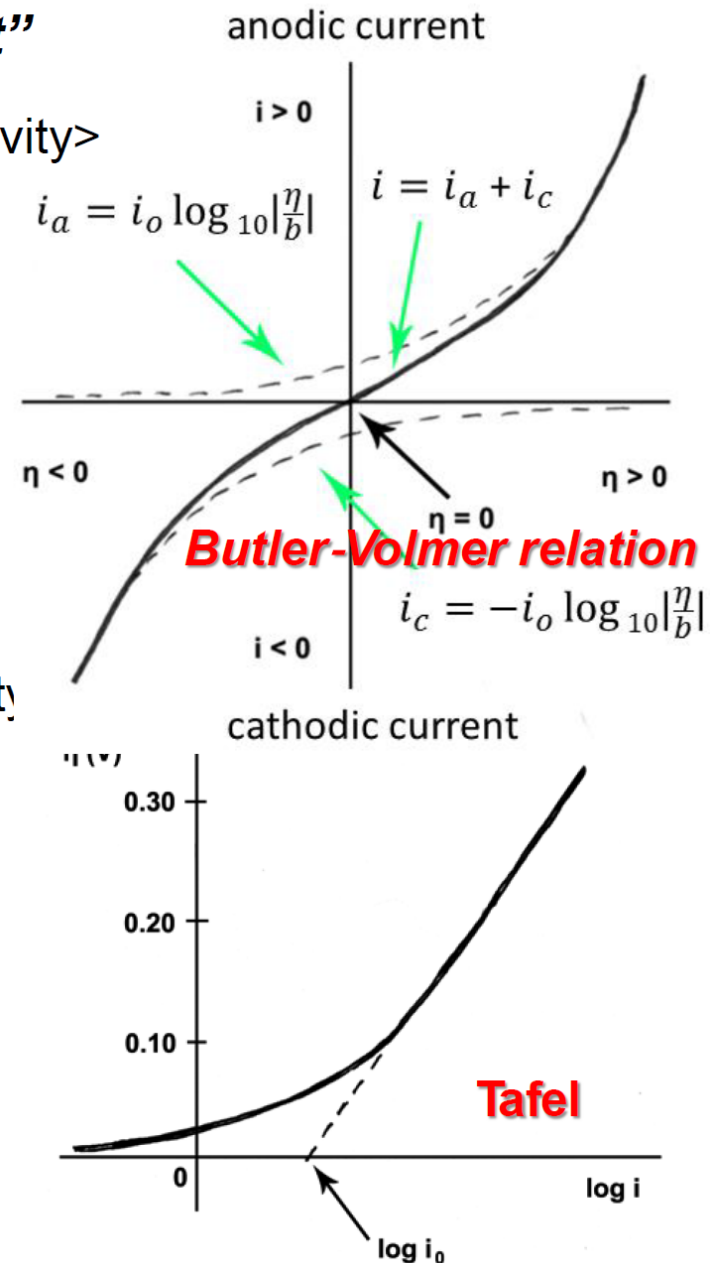
Electrochemical reaction : “Figures of merit”

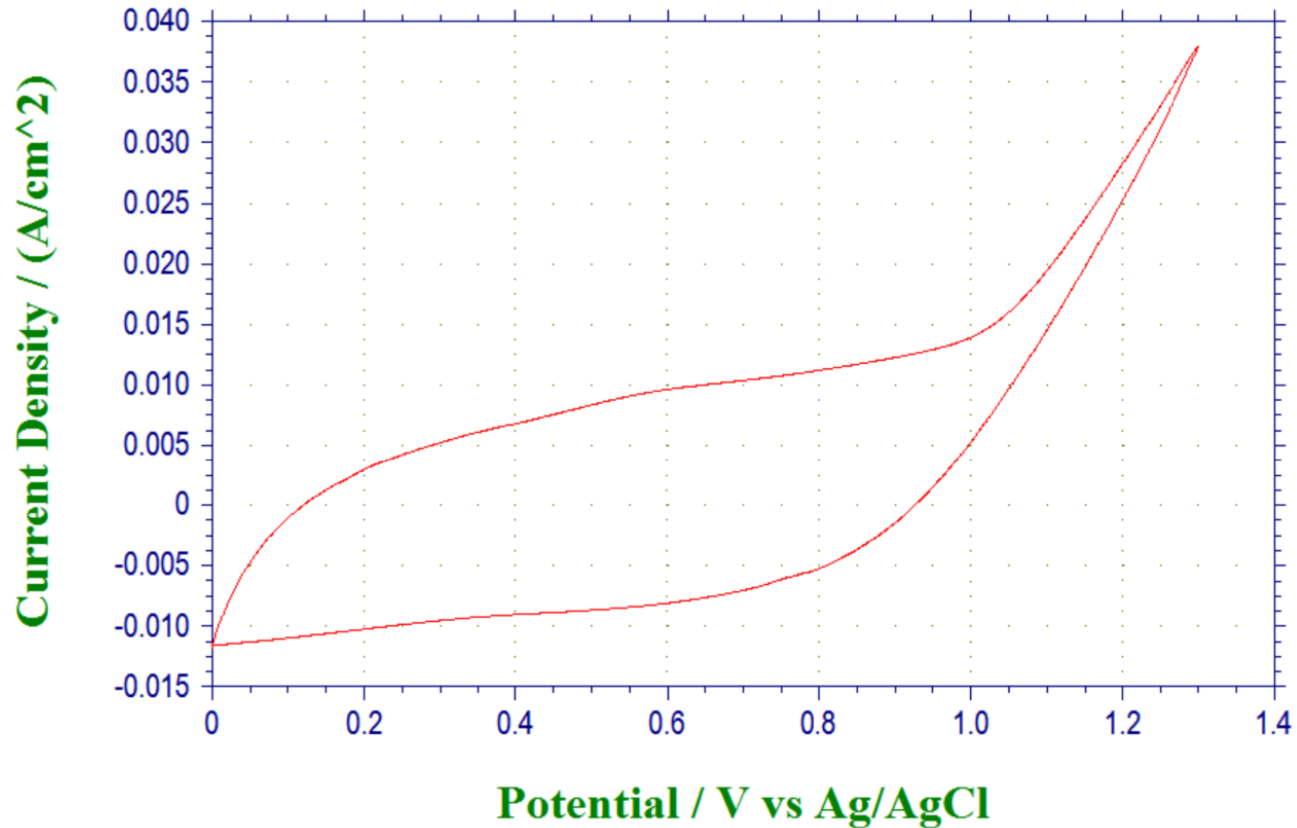
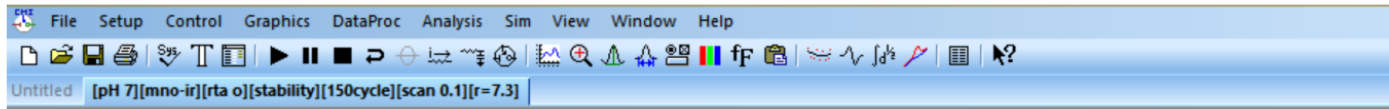
<Four primary figures of merit for electrocatalyst activity>

- Exchange current density, i_0 (mA/cm²)
- Tafel slope, b (mV/decade)
- Current density at a given overpotential:
: $J_{E(V \text{ vs. RHE})}$ (mA/cm²)
- Overpotential needed to reach a given current density
: η (mV) @10mA/cm²

<Three ways to report current density>

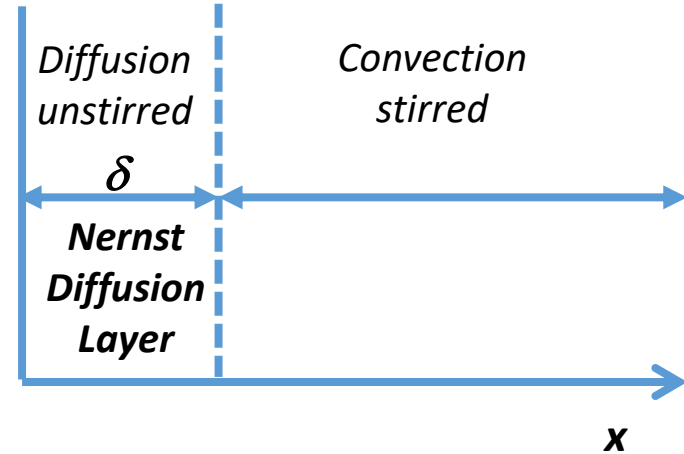
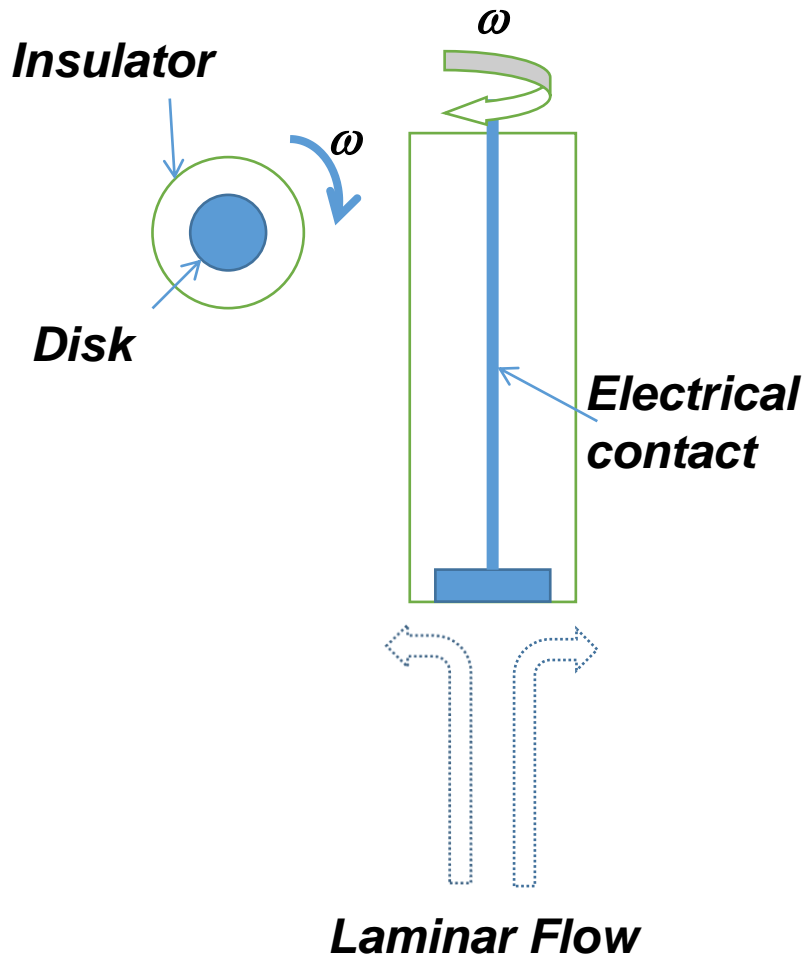
- Per geometric area (cm_{geo}²)
- Per surface area (cm_{real}²)
- Per electrochemically active surface area (cm_{ECSA}²)





**How can we analyze the electrochemical data?
What kind of information can we obtain?**

Mass Transfer in RDE



$$J_i(x) = -D_i \frac{dC_i(x)}{dx} + C_i v(x)$$

$$v(x) \propto \omega^{3/2} x^2$$

if x small, $v(x) \approx 0$

if x small, $v(x) \approx 0$: Diffusion > Convection

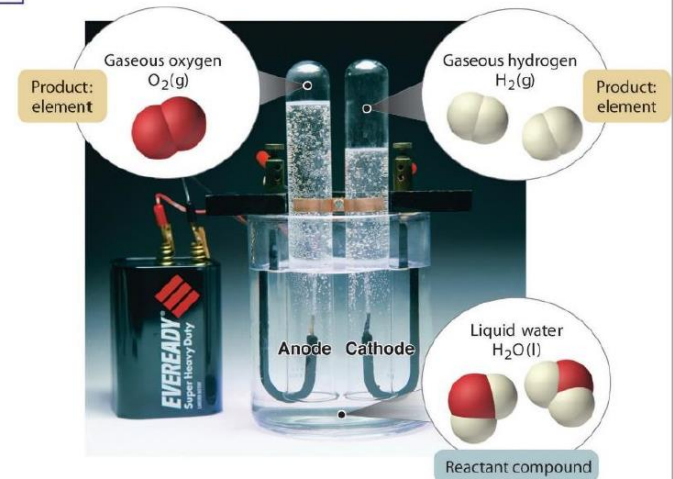
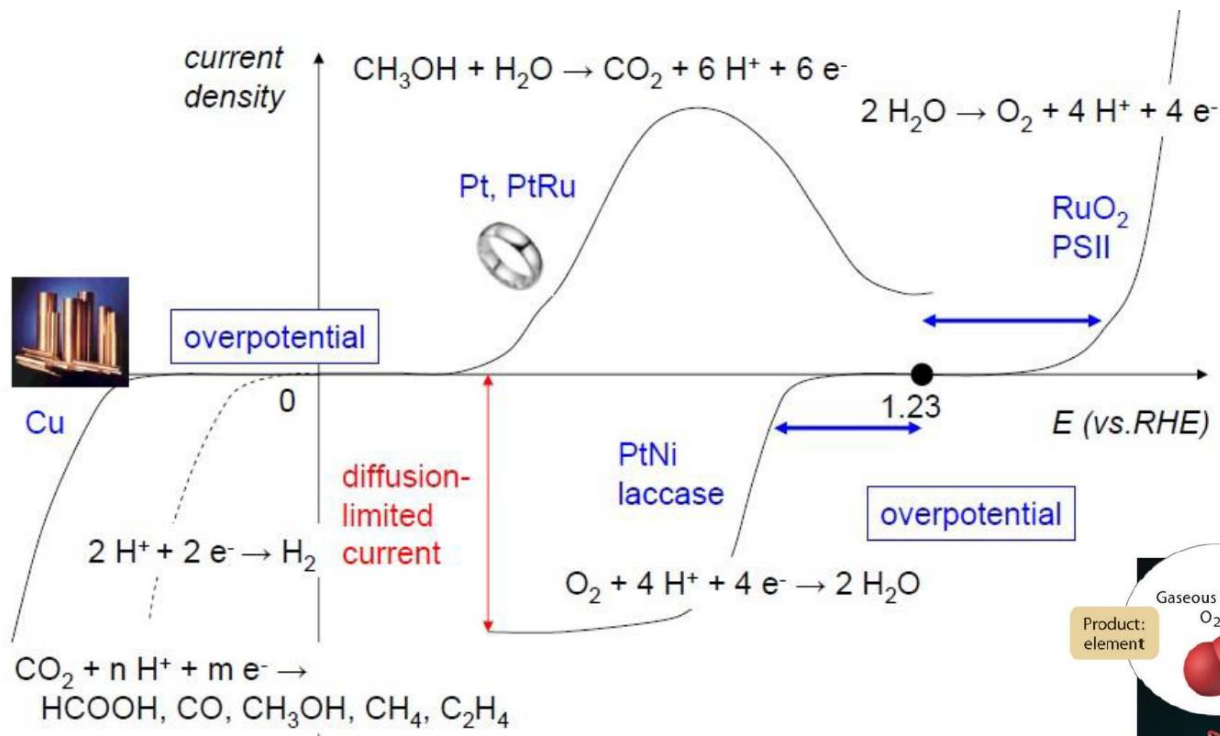
if x large, : Diffusion < Convection

Nernst Diffusion Layer $\delta = 1.61 D_i^{1/3} \nu^{1/6} / \omega^{1/2}$

ω : angular velocity

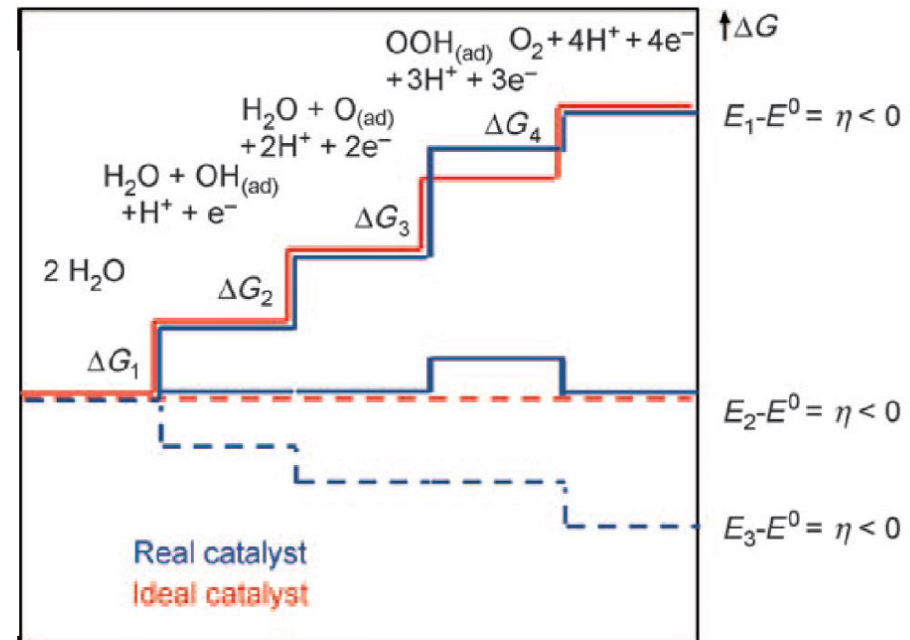
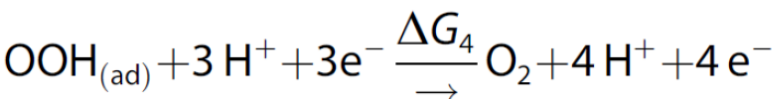
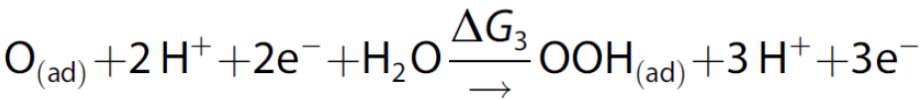
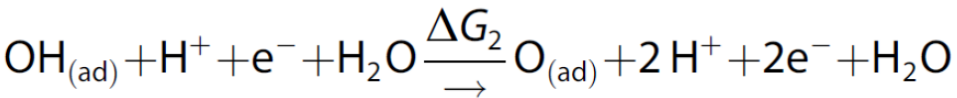
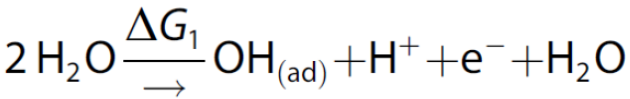
ν : kinematic viscosity $\sim 0.01 \text{ cm}^2/\text{s}$ for aqueous sol'n

Application : Electrochemical water splitting



Of the two half reactions, OER is considerably more difficult because it requires a four-electron oxidation of two water molecules coupled to the removal of four protons to form a relatively weak O=O bond. → Efficient OER catalyst is required!

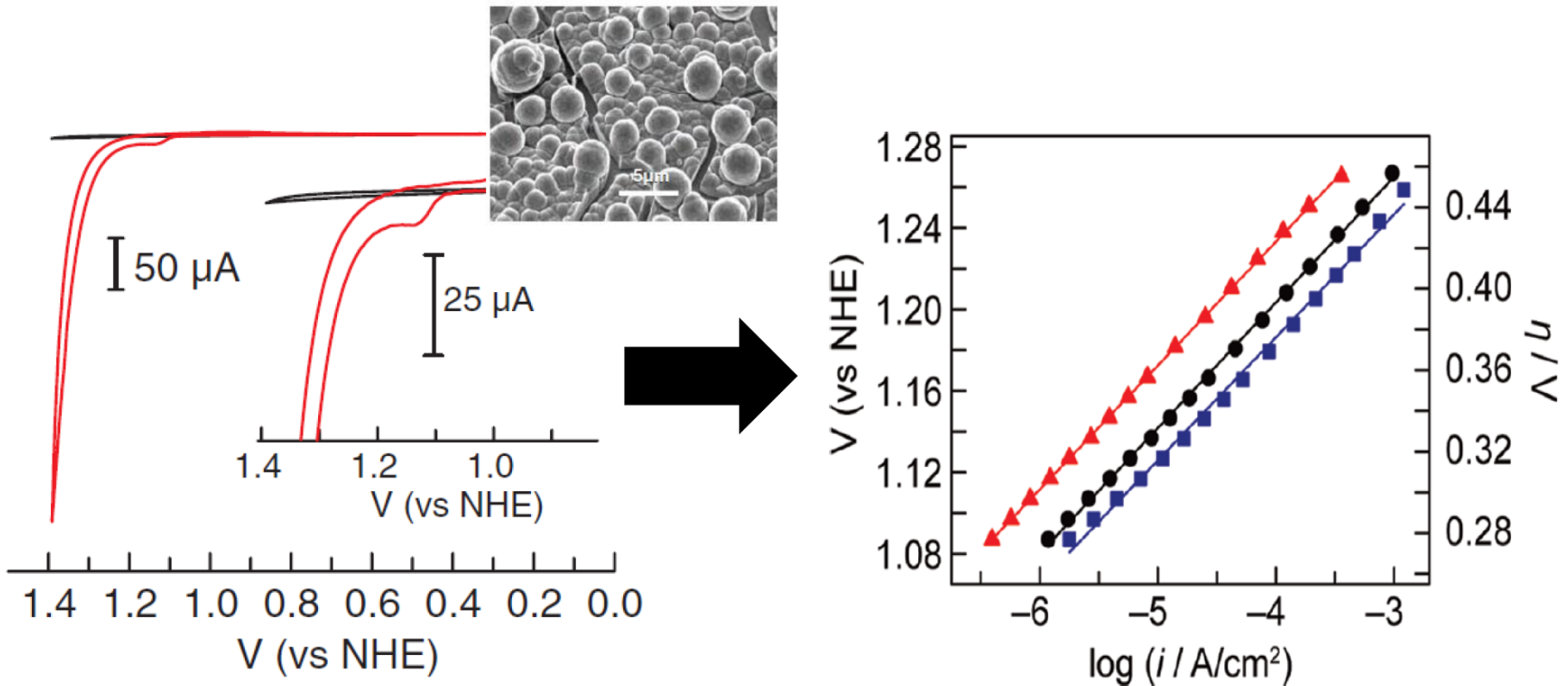
Theoretical point of view: 4 steps in water oxidation reaction



Anodic reaction : Water oxidation reaction

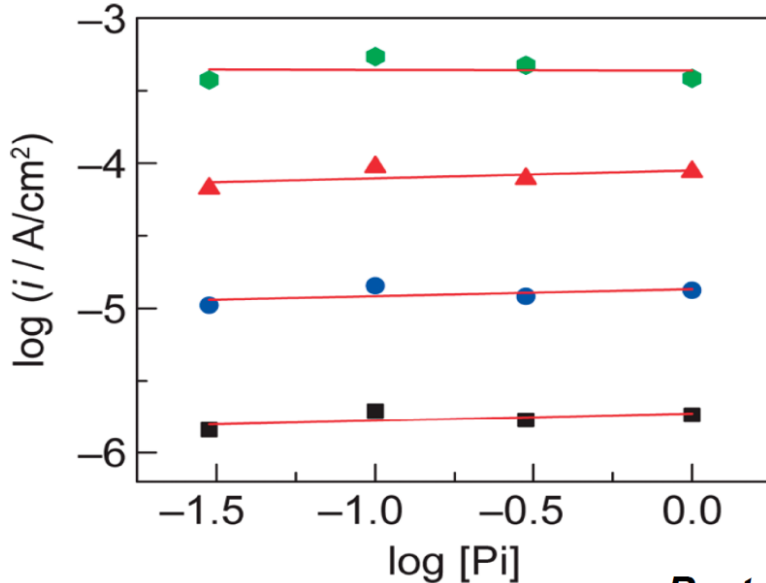
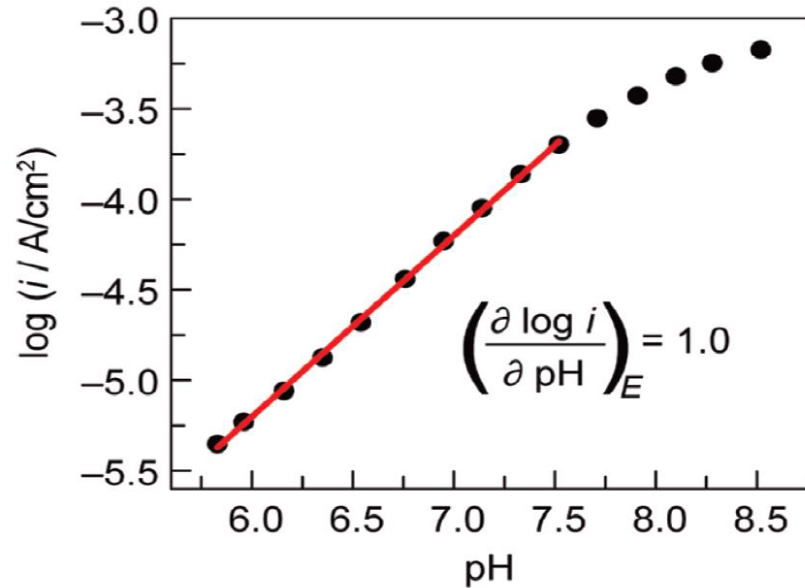
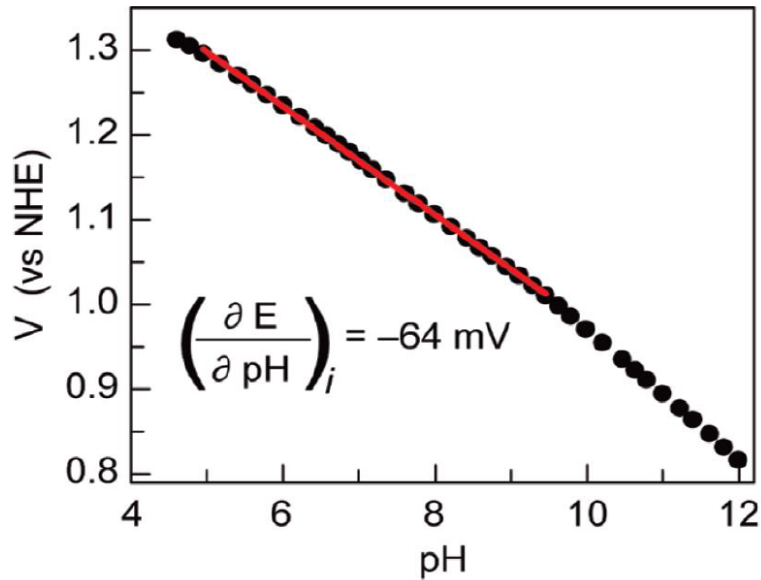
- Total 4 electrons and 4 protons are involved in this reaction.
- Thermodynamic potential for water oxidation is 1.23 V vs. NHE.
- Overall change in free energy of the four electron water splitting reaction amounts to 4.92 eV
- Taking water as the zero point of the energy scale, the Gibbs energies of adsorption of the ideal intermediates would be 1.23 eV, 2.46 eV, and 3.69 eV for $\text{OH}_{(\text{ad})}$, $\text{O}_{(\text{ad})}$, and $\text{OOH}_{(\text{ad})}$, respectively.

Water Oxidation: Tafel plot and pH dependency



- [I-V curve] can be transformed into [Log J vs V] to get the Tafel plot.
- In order to minimize the non-faradaic current, bulk electrolysis at the designed potential was performed for certain time.
- Tafel plot is only validated near the small overpotential region where surface coverage can be assumed to zero.

Water Oxidation: Tafel plot and pH dependency



$$\left(\frac{\partial E}{\partial \text{pH}}\right)_i = -\left(\frac{\partial E}{\partial \log(i)}\right)_{\text{pH}} \left(\frac{\partial \log(i)}{\partial \text{pH}}\right)_E$$

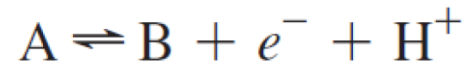
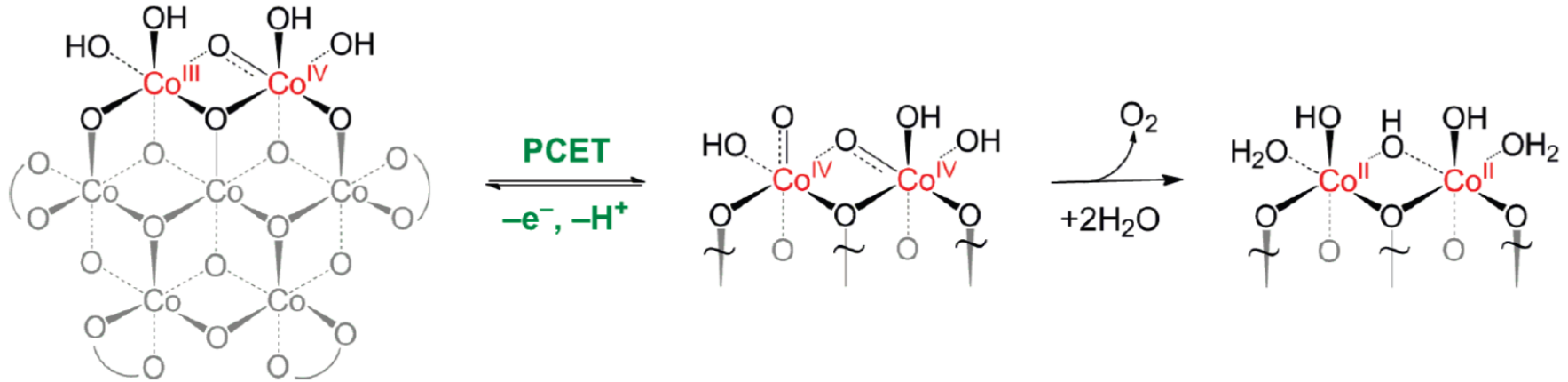
$$\alpha = -\left(\frac{2.3RT}{F}\right) \left(\frac{1}{b}\right)$$

α = Transfer coefficient, b = Tafel slope

$$\left(\frac{\partial \log j}{\partial \log a_{\text{H}^+}}\right)_E = -\left(\frac{\partial \log j}{\partial \text{pH}}\right)_E$$

23
Proton reaction order can be obtained from pH dependency

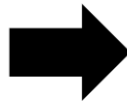
Water Oxidation: Tafel plot and pH dependency



Transfer coefficient (α) = '1'

Proton reaction order = '1'

No buffer dependency



B → C : Rate determining step

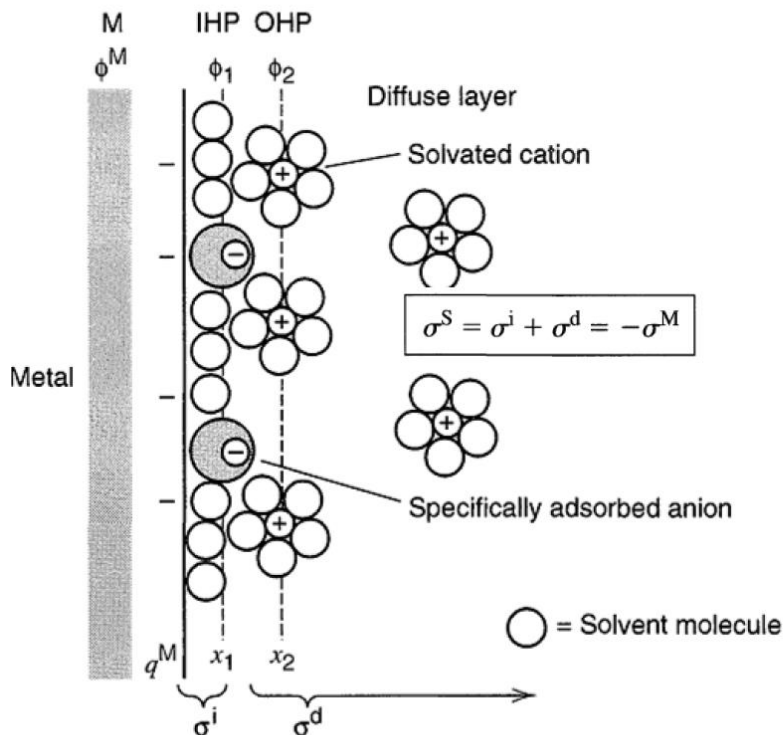
$$i = k_0(a_{H^+})^{-1} \exp\left[\frac{FE}{RT}\right]$$

- From the electrochemical study, we can say "1 electron and 1 proton involved pre-equilibrium step exist before RDS"
- Further verification by spectroscopic analysis is needed to verify the detailed reaction species and metal valency change during catalysis .

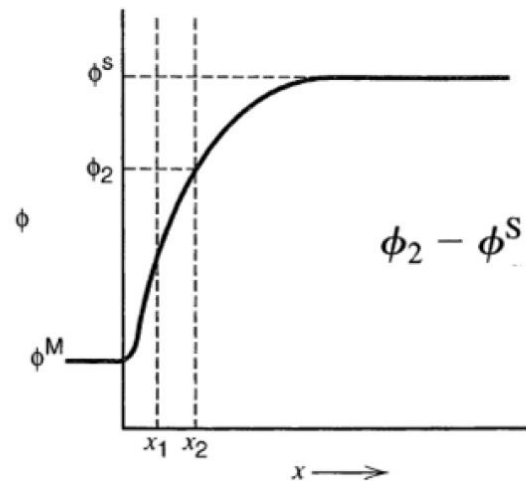
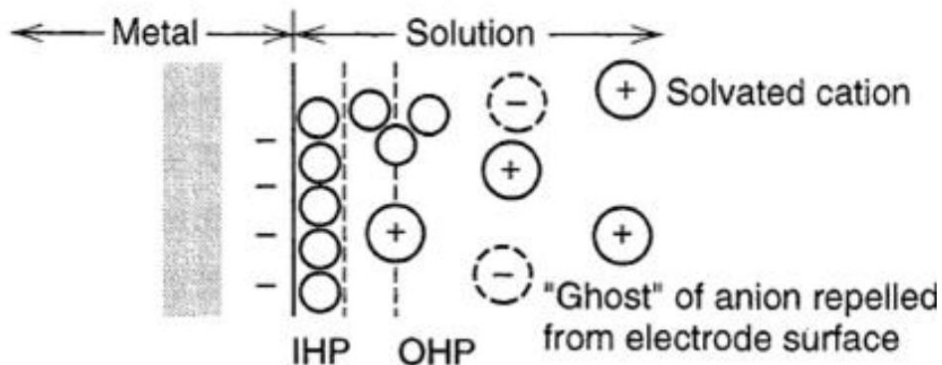
Non-faradaic processes and the nature of the electrode-solution interface

- Faradaic Process vs. Nonfaradaic process
- Faradaic process : charge transfer across the metal(electrode)-solution interfaces (governed by Faradaic law)
→ Charge transfer process
- Nonfaradaic process : the variation of current caused by adsorption and desorption of molecules without charge transfer
- Ideal Polarized Electrode(IPE)
- An electrode at which no charge transfer can occur across the metal-solution interface
- While no real electrode can behave as an IPE over the whole potential range available in a solution, some electrode-solution systems can approach ideal polarizability over limited potential ranges.
- The nonfaradaic current is dominant at ideal polarized region

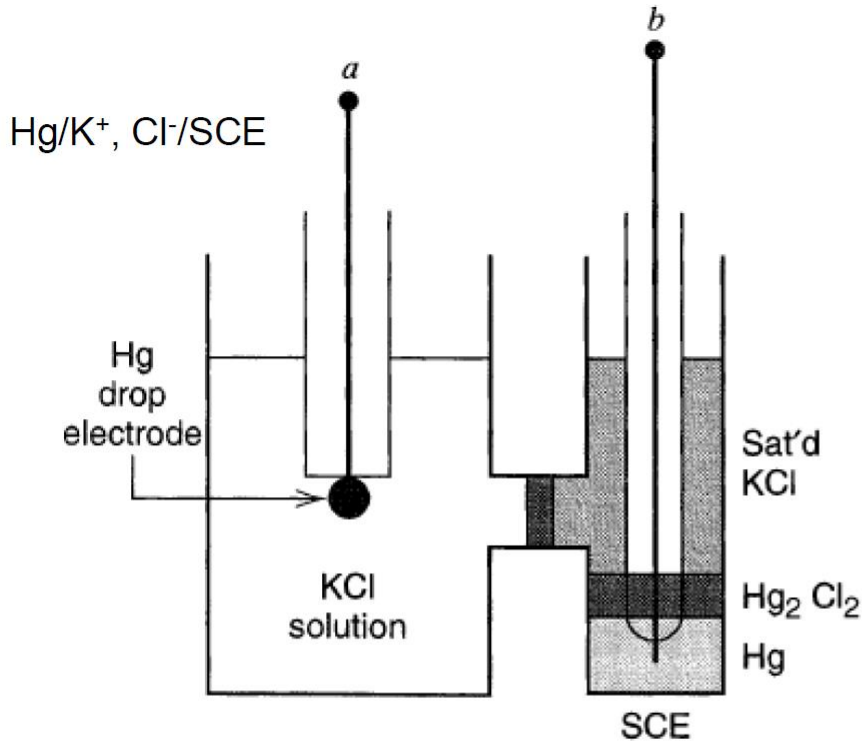
Electric Double Layer



- **Electrical Double Layer :**
Array of charged species and oriented dipoles existing at the metal-solution interface
- **Inner Helmholtz Plane(IHP) :**
Adsorbed ions on electrical centers
- **Outer Helmholtz Plane(OHP) :**
Adsorbed nearest solvated ions
- **Diffuse Layer :**
Extends of OHP into the bulk of solution



Double-Layer Capacitance and Charging Current in Electrochemical Measurements



C_d : electrode / electrolyte interface capacitance

R_s : resistance between electrolyte

C_{SCE} : reference electrode / electrolyte interface capacitance

C_T : Total capacitance

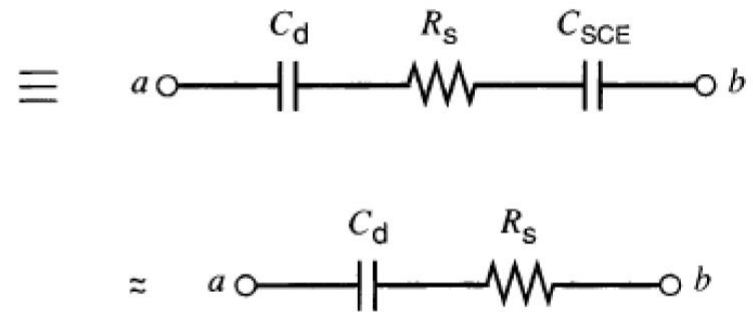


Figure 1.2.5 *Left:* Two-electrode cell with an ideal polarized mercury drop electrode and an SCE. *Right:* Representation of the cell in terms of linear circuit elements.

$$C_T = \frac{C_d C_{SCE}}{[C_d + C_{SCE}]} \quad \longrightarrow \quad C_{SCE} \gg C_d \quad \longrightarrow \quad C_T \approx C_d$$

Response of Current, Voltage at Double Layer of Electrochemical Cell

Voltage Step (Current Response)

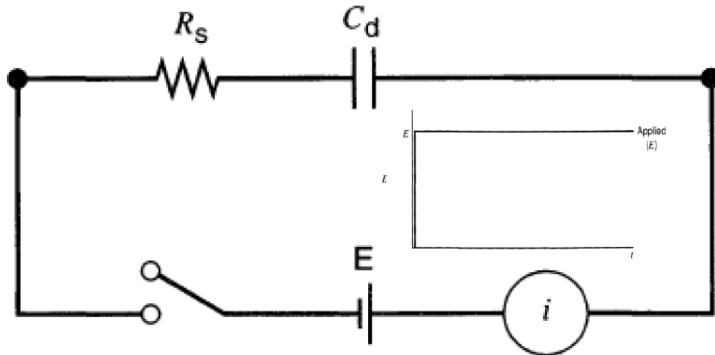
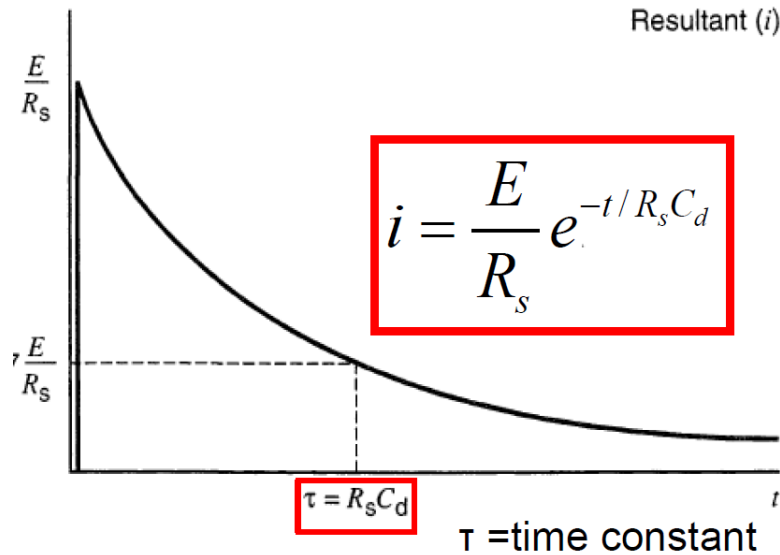
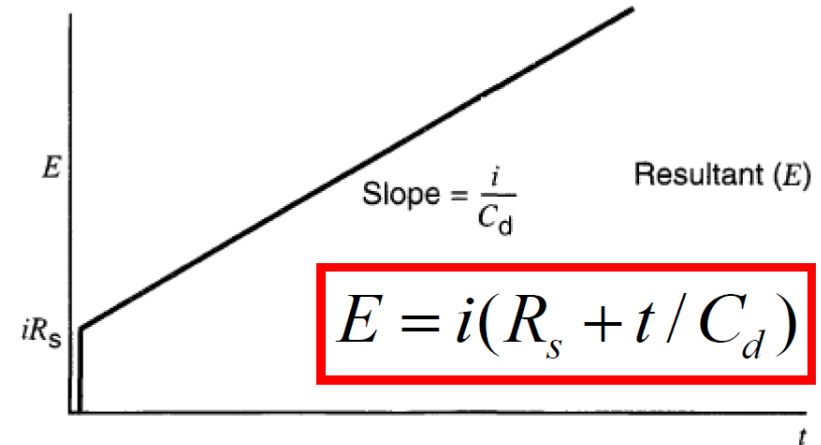
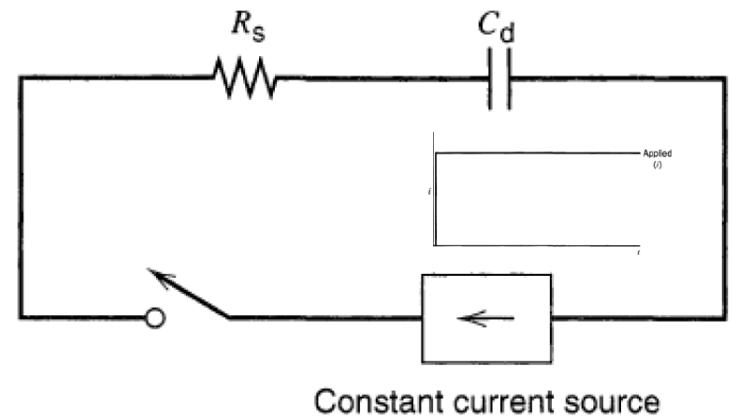


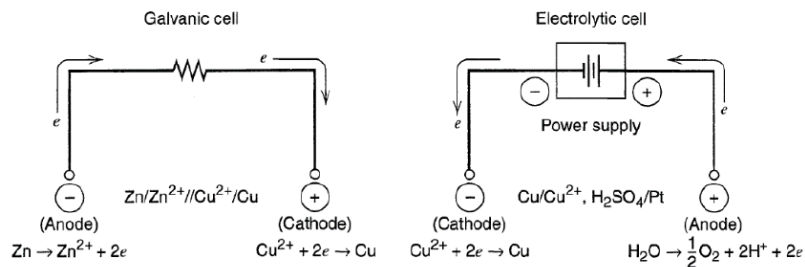
Figure 1.2.6 Potential step experiment for an RC circuit.



Current Step (Voltage Response)



Faradaic Processes and Factors Affecting Rates of Electrode Reaction



Electrochemical cell

Galvanic cell : reactions occur spontaneously at the electrodes

Electrolytic cell : reaction is effected by the imposition of an external voltage greater than open-circuit potential

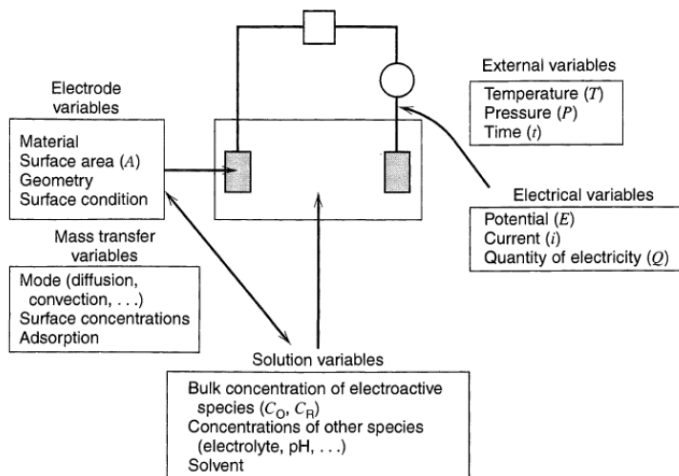


Figure 1.3.2 Variables affecting the rate of an electrode reaction.

$$i \text{ (amperes)} = \frac{dQ}{dt} \text{ (coulombs/s)}$$

$$\frac{Q}{nF} \text{ (coulombs/mol)} = N \text{ (mol electrolyzed)}$$

$$\text{Rate (mol/s)} = \frac{dN}{dt} = \frac{i}{nF}$$

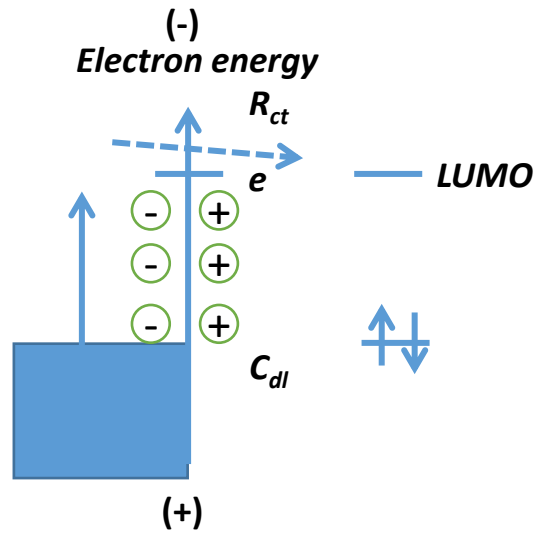
$$\text{Rate (mol s}^{-1} \text{ cm}^{-2}) = \frac{i}{nFA} = \frac{j}{nF}$$

The departure of the electrode potential (or cell potential) from the equilibrium value upon passage of faradaic current is termed polarization. The extent of polarization is measured by the overpotential, η

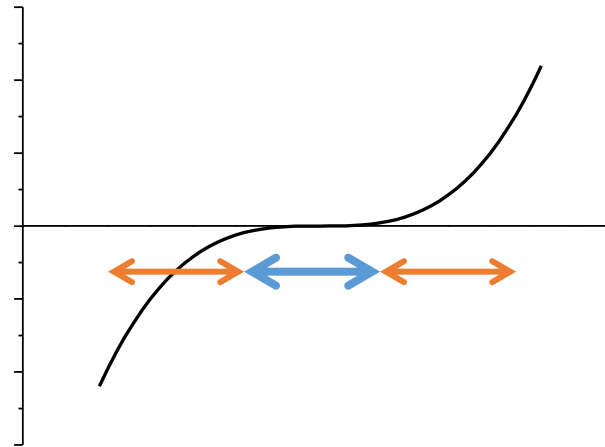
$$\eta = E - E_{eq}$$

Thermodynamics & Kinetics for Electrolysis

Definition of R_{ct} & C_{dl}



Faradaic & non-Faradaic Current



Faradaic current:

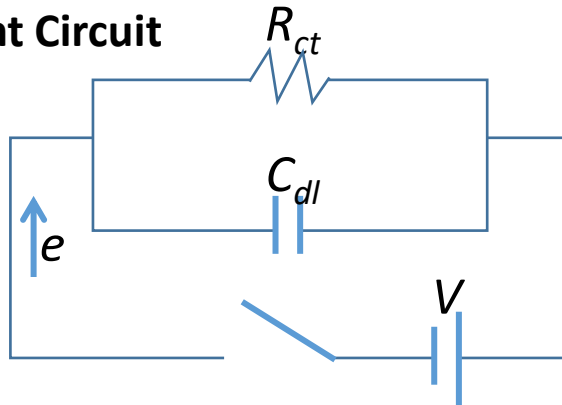
Current used for $O + ne \rightarrow R$ reaction



Non-faradaic current :

Charging curr. & etc.,

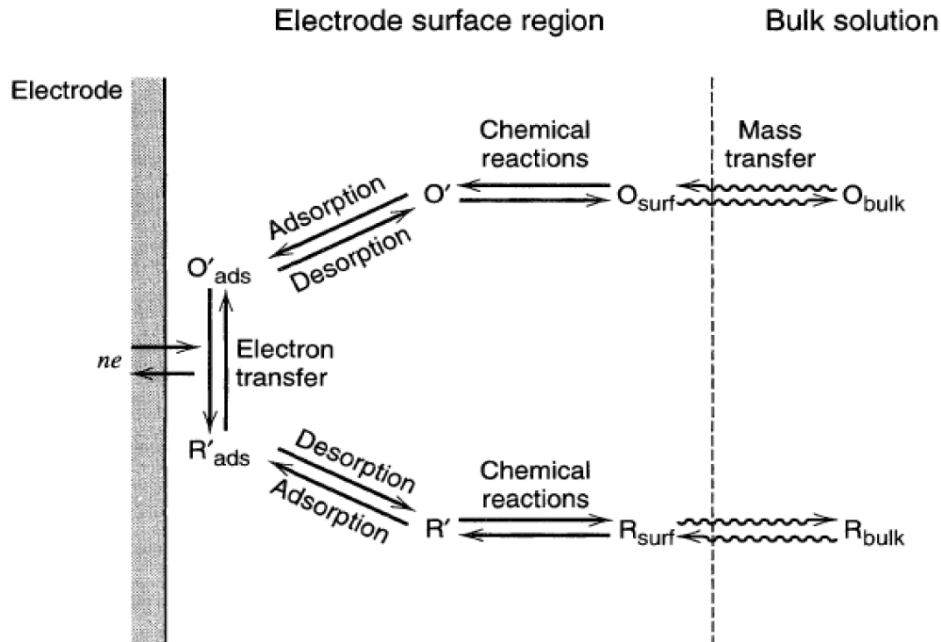
Equivalent Circuit



R_{ct} : Charge transfer resistance

C_{dl} : Electric double-layer capacitance

Factors Effecting Electrode Reaction Rate and Current



1. Mass transfer (e.g., of O from the bulk solution to the electrode surface).
2. Electron transfer at the electrode surface
3. Chemical reactions preceding or following the electron transfer. These might be homogeneous processes (e.g., protonation or dimerization) or heterogeneous ones (e.g., catalytic decomposition) on the electrode surface
4. Other surface reactions, such as adsorption, desorption, or crystallization (electrodeposition).

Electrochemical Cells and Cell Resistance

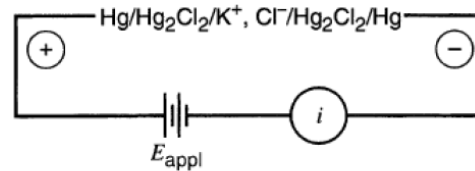
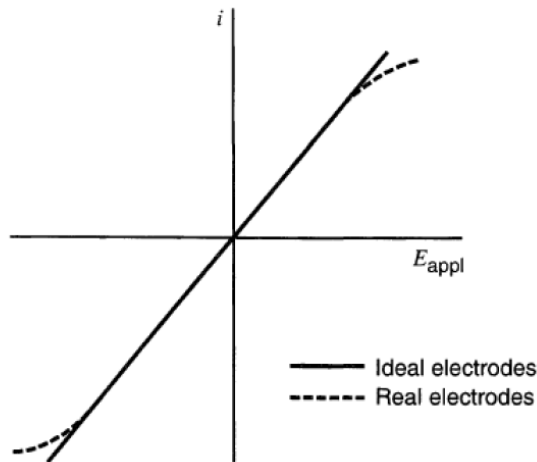


Figure 1.3.8 Current-potential curve for a cell composed of two electrodes approaching ideal nonpolarizability.

- Polarization curve : Current-potential curves, particularly those obtained under steady-state conditions called polarization curves
- When potential of electrode is measured against nonpolarizable reference electrode during the passage of current, a voltage drop equal to iR_s is always included
- R_s : solution resistance between the electrodes unlike the impedances describing the mass transfer and activation steps in the electrode reaction

$$E_{\text{appl}} (\text{vs. SCE}) = E_{\text{Cd}}(\text{vs. SCE}) - iR_s = E_{\text{eq,Cd}}(\text{vs. SCE}) + \eta - iR_s$$

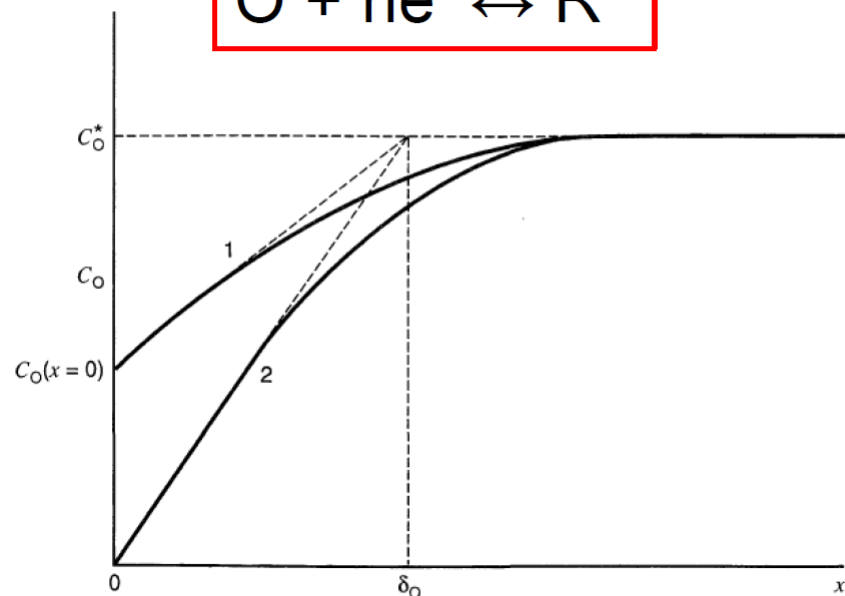
Introduction to Mass-Transfer-Controlled Reactions

- Electrode process involves only fast heterogeneous charge-transfer
 - (a) homogeneous reactions=equilibrium
 - (b) surface concentrations involved in the faradaic process related to the electrode potentials
- The net rate of the electrode reaction $v_{\text{rxn}}=v_{\text{mt}}=i/nFA$

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

- **The modes of mass transfer:**
 1. Migration. Movement of a charged body under the influence of an electric field (a gradient of electrical potential)
 2. Diffusion. Movement of a species under the influence of a gradient of chemical potential (i.e., a concentration gradient)
 3. Convection. Stirring or hydrodynamic transport. Generally fluid flow occurs because of natural convection (convection caused by density gradients) and forced convection, and may be characterized by stagnant regions, laminar flow, and turbulent flow.

Steady-State Mass Transfer



- Once electrolysis of species O begins, its concentration at the electrode surface, $C_O(x=0)$ becomes smaller than the value, C_O^* , in the bulk solution (far from the electrode)
- Assumes a linear concentration gradient within the diffusion layer,

$$v_{\text{mt}} \propto (dC_O/dx)_{x=0} = D_O(dC_O/dx)_{x=0}$$

- Since δ_O is often unknown, let $M_O = D_O/\delta_O$

$$v_{\text{mt}} = D_O[C_O^* - C_O(x=0)]/\delta_O$$

$$v_{\text{mt}} = m_O[C_O^* - C_O(x=0)]$$

$$\frac{i}{nFA} = m_O[C_O^* - C_O(x=0)]$$

- Stirring is ineffective at the electrode surface
→ solution velocity not considered at $x=0$
- Mass transfer rate
 \propto concentration gradient on electrode

$$v_{\text{mt}} = D_O(dC_O/dx)_{x=0}$$

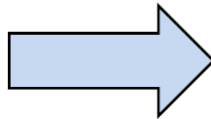
Steady-State Mass Transfer (continued)

The values of $C_O(x=0)$ and $C_R(x=0)$ are functions of electrode potential, E . The largest rate of mass transfer of O occurs when $C_O(x=0) = 0$. The value of the current under these conditions is called the *limiting current*, i_l

$$i_l = nFAm_O C_O^*$$

$$\frac{C_O(x=0)}{C_O^*} = 1 - \frac{i}{i_l}$$

$$C_O(x=0) = \frac{i_l - i}{nFAm_O}$$



If the electron transfer is **rapid**, the concentration of O and R at the electrode surface can be governed with Nernst equation

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{C_O(x=0)}{C_R(x=0)}$$

Transient Response

- Consider diffusion layer as time dependent function

$$i/nFA = v_{mt} = D_O [C_O^* - C_O(x=0)]/\delta(t)$$

$$\frac{[C_O^* - C_O(x=0)] A d\delta(t)}{2} = \frac{i}{nF} = \frac{D_O A}{\delta(t)} [C_O^* - C_O(x=0)] \xrightarrow{\delta(t) = 2\sqrt{D_O t}} \frac{i}{nFA} = \frac{D_O^{1/2}}{2t^{1/2}} [C_O^* - C_O(x=0)]$$

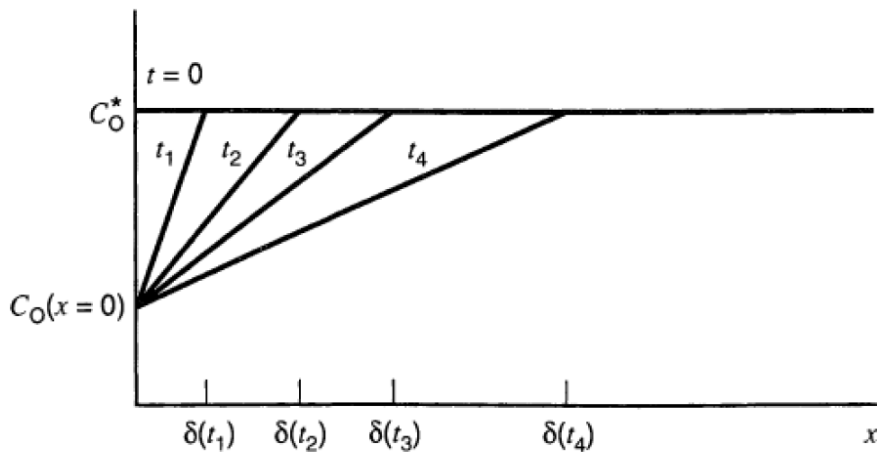


Figure 1.4.5 Growth of the diffusion-layer thickness with time.

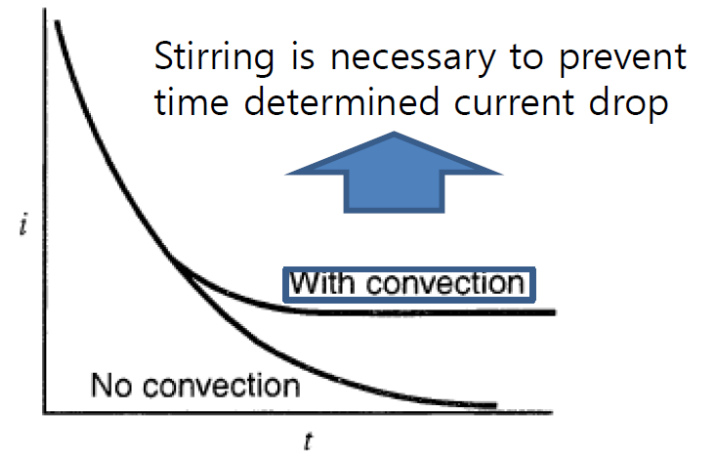
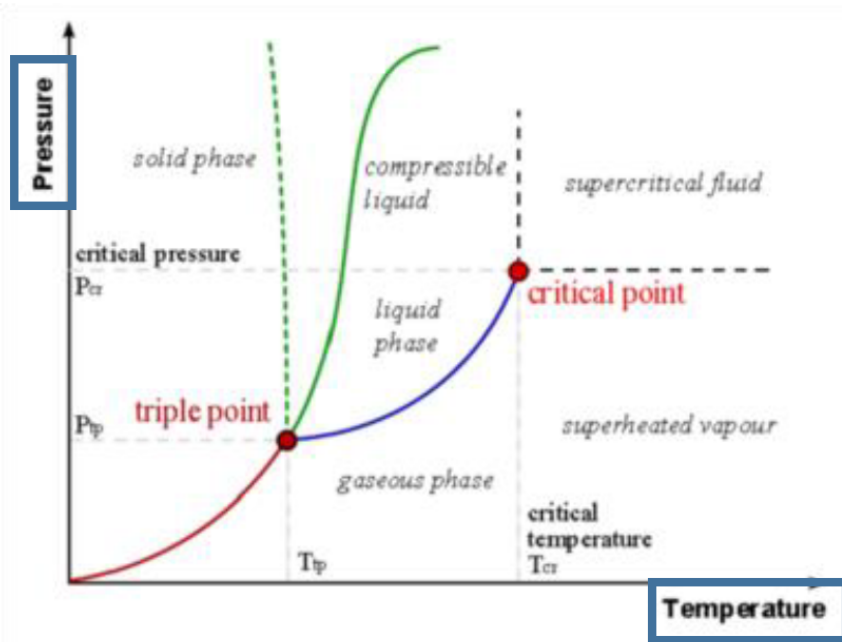


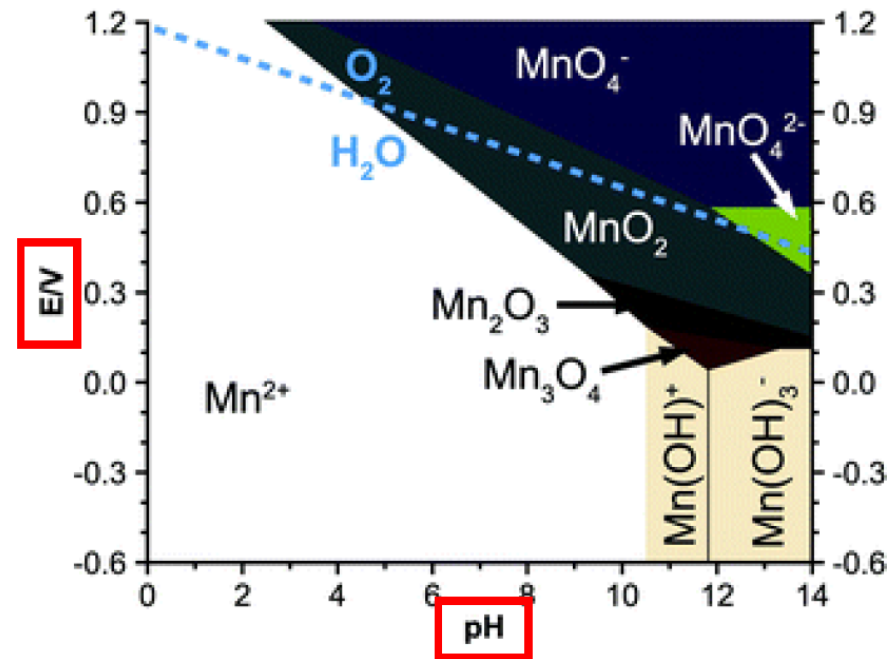
Figure 1.4.6 Current-time transient for a potential step to a stationary electrode (no convection) and to an electrode in stirred solution (with convection) where a steady-state current is attained.

Pourbaix Diagram

- In chemical thermodynamics, a phase is defined by **T, P,** and **composition (concentration)**
- In electrochemical thermodynamics, a phase is defined by **T, P, composition** and **emf**.
- Equilibria Diagram in..
 - Chemical system : p-T-composition phase diagram
 - Electrochemical system : **emf-pH diagram (Pourbaix diagram)**



Chemical System
(P-T-composition diagram)



Electrochemical System
(emf-pH diagram)

Pourbaix Diagram on Materials Project

Generates stability diagrams in aqueous solutions using our database of DFT calculations on solids, and experimental data on ions in solution

Element (optional) (optional)

Fe Cr Generate

Select up to 3 elements. H and O are included by default.

Concentration in mol/kg

0 Fe 1e-8 1

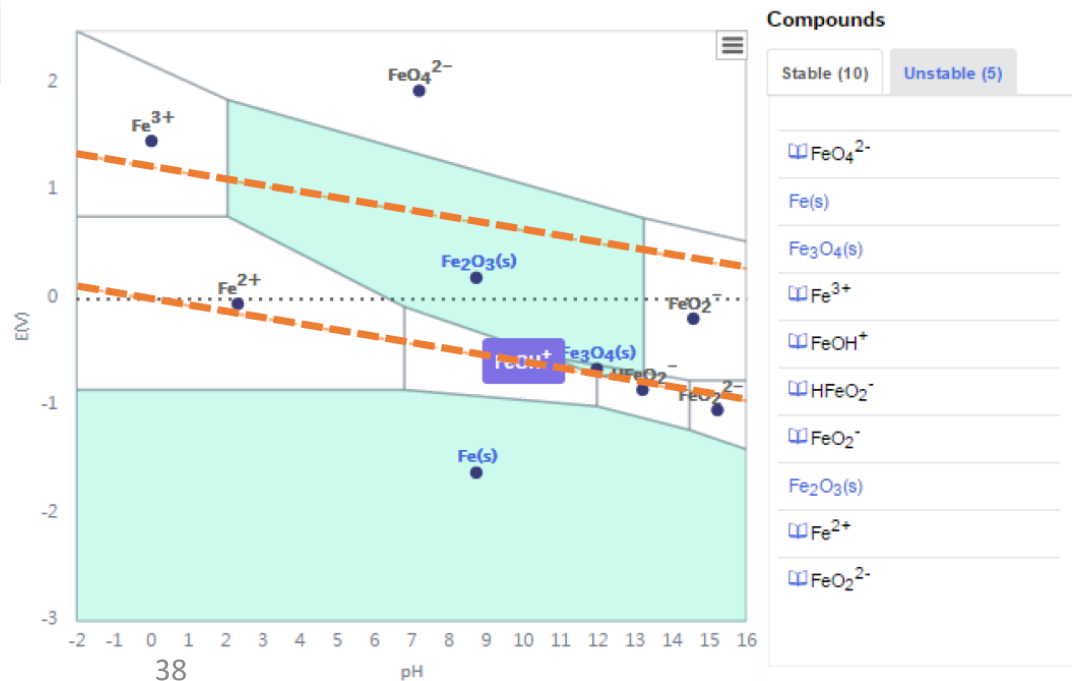
Select Elements

Change concentration

< Materials Project >

Able to draw Pourbaix diagrams of selected elements

www.materialsproject.org



Thank you