Schedule

[Fundamentals]

1. 4/15 Basic chemical and biochemical concepts
2. 4/22 Basic biophysical concepts
3. 4/29 Basic bioelectrochemical concepts1
4. 5/13 Basic bioelectrochemical concepts2

[Applications]

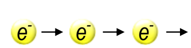
5. 5/20 Cancel (Homework1 and 2)
6. 5/27 Biosensors and bioelectronics1
7. 6/03 Cancel (Homework3 and 4)
8. 6/10 Student seminar
9. 6/17 Biosensors and bioelectronics2
10. 6/24 From bioelectronics (electron) to iontronics (ion)1
11. 7/01 From bioelectronics (electron) to iontronics (ion)2
12. 7/ 8 Wearable applications1
13. 7/15 Wearable applications2
14. 7/22 Student seminar

Principle of electrochemistry

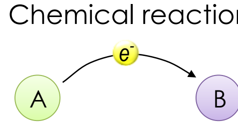
The relationship between chemical reaction and electricity
(Conversion: chemical energy ⇆ electrical energy)

Electricity

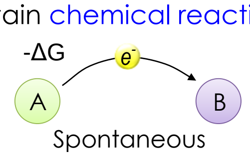
movement of electrons



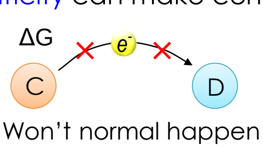
Chemical reaction

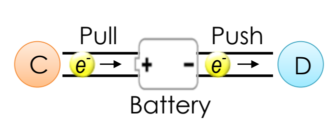


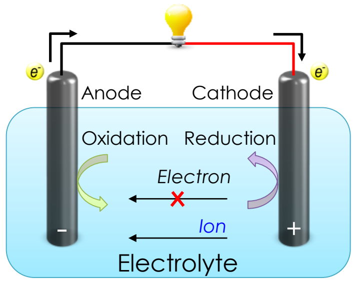
1. Certain chemical reactions can create electricity. (Galvanic cell)



2. Electricity can make certain chemical reactions. (Electrolytic cell)

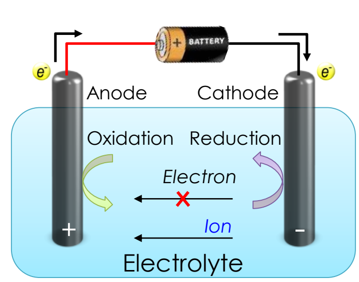






Galvanic cell

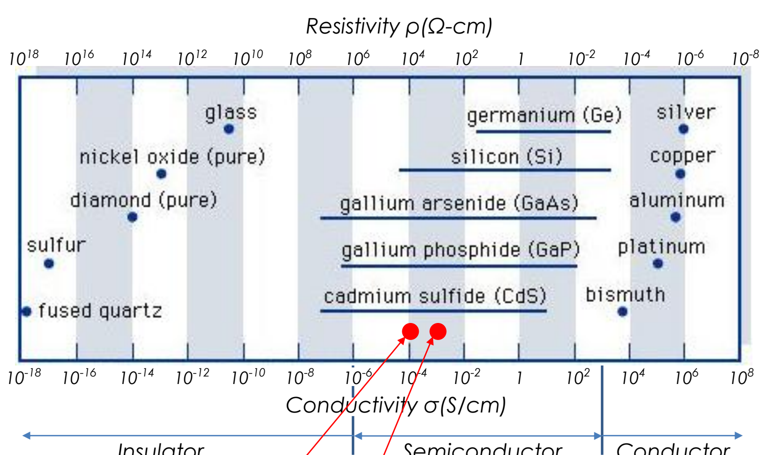
$$V \cong IR$$



Electronic cell

Galvanic cell		Electronic cell
External circuits(Electron) Electrolyte( ) Electrode(Ion)	**Resistance**	External circuits(Electron) Electrolyte(Ion conductivity) Electrode(Ion)
	Voltage	Power supply Electrochemical potential (in battery)
	Current	

Conductivity (σ)



Proton (H^+): 10^{-3} S cm^{-1}

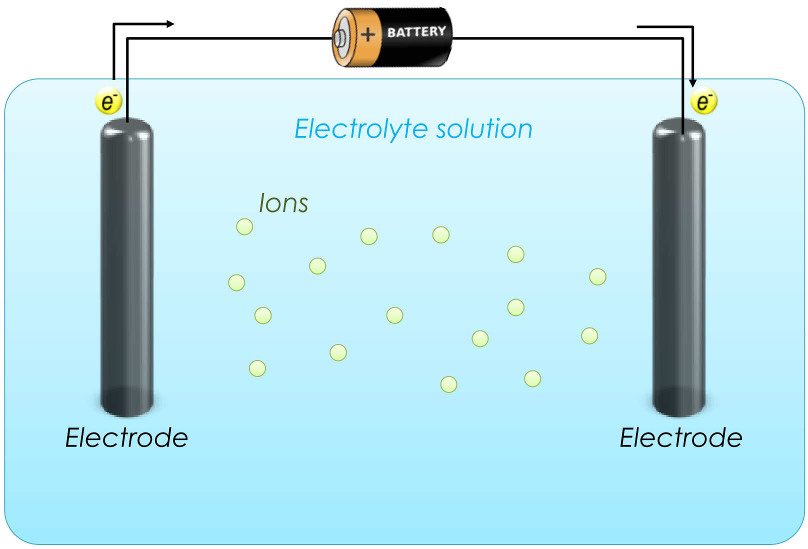
Sodium ion (Na^+): 10^{-4} S cm^{-1}

Ionic conductivity (σ)

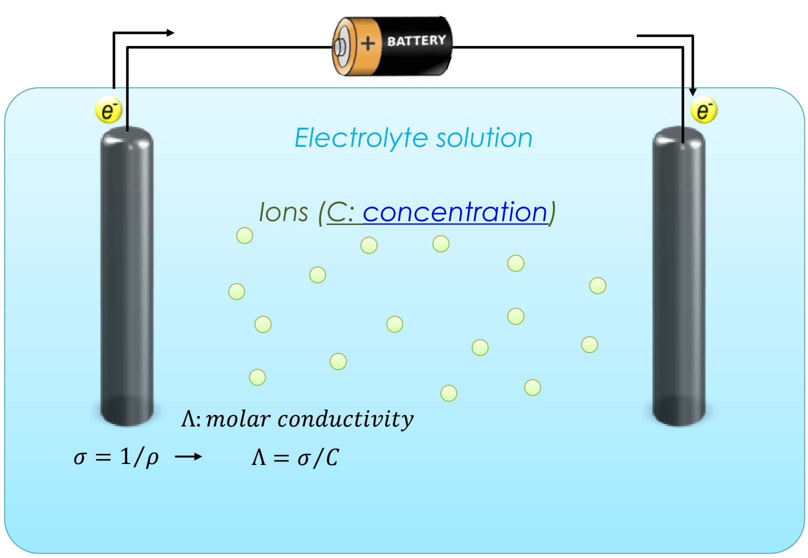
$$V = IR$$
$$= I(l/A)\rho$$

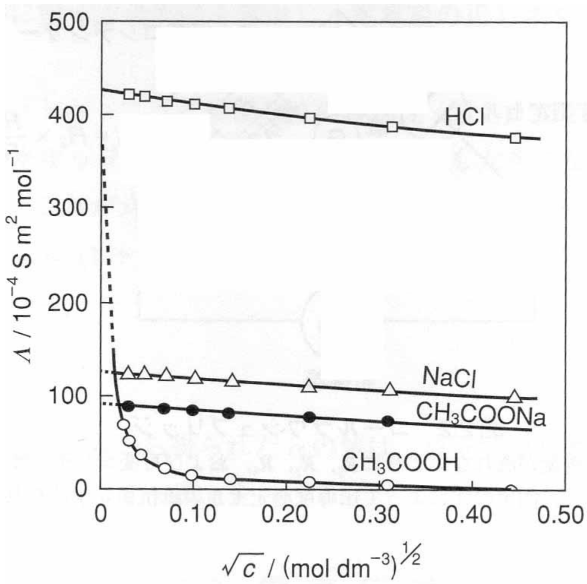
$$\boxed{\sigma = 1/\rho}$$

A: Electrode area
ρ: Resistivity
l: Length between electrodes



Ionic conductivity (σ)



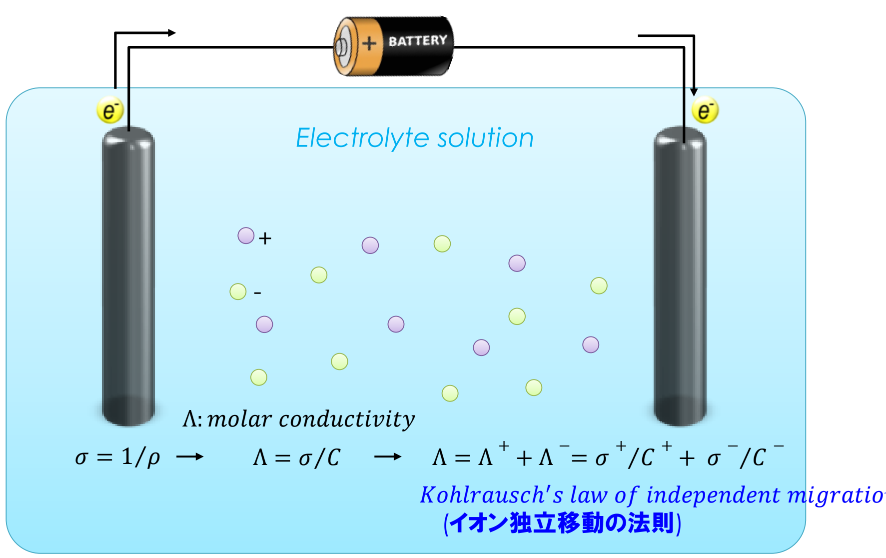


モル電気伝導率と電解質濃度の平方根の関係

図2.4　大堺ら「ベーシック電気化学」（化学同人）

$$\Lambda \neq \frac{\sigma}{c}$$

Ionic conductivity (σ)



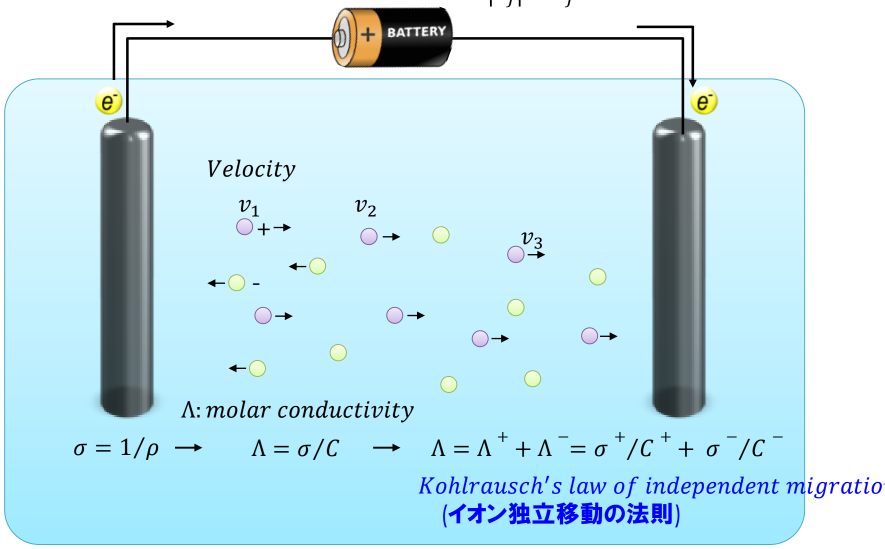
Ionic conductivity (σ)

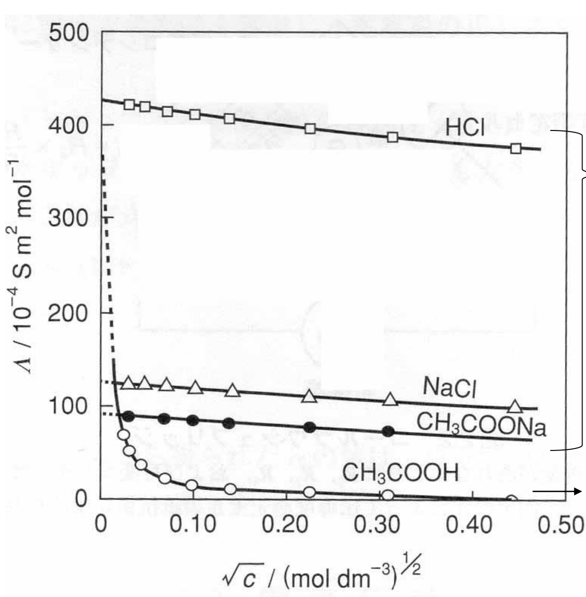
$$I_j = |Z_j| e \cdot n_j v_j \ (From\ motion\ equation)$$

$$\sigma_j = |Z_j| e \cdot n_j \mu_j$$

μ_j: Mobility

$|Z_j| e \cdot n_j$: Carrier





モル電気伝導率と電解質濃度の平方根の関係

図2.4　大堺ら「ベーシック電気化学」（化学同人）

electrolytes

Kohlrausch's law

electrolytes

Ostwald's dilution law

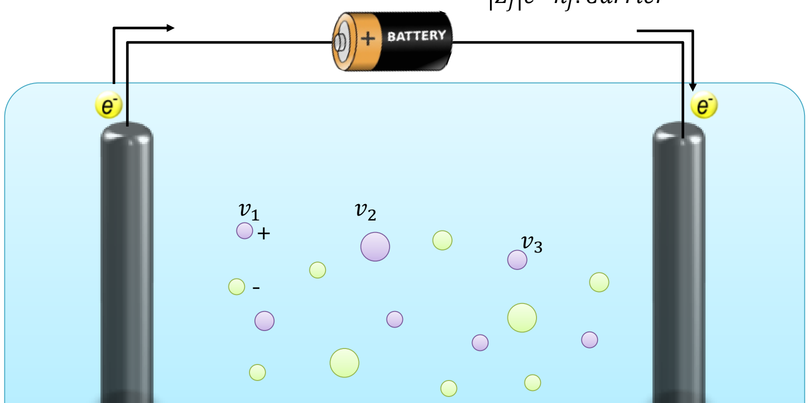
Ionic conductivity (σ)

$$I_j = |Z_j| e \cdot n_j v_j \ (From\ motion\ equation)$$

$$\sigma_j = |Z_j| e \cdot n_j \mu_j$$

μ_j: Mobility

$|Z_j| e \cdot n_j$: Carrier



Λ: molar conductivity

$$\sigma = 1/\rho \longrightarrow \Lambda = \sigma/C \longrightarrow \Lambda = \Lambda^+ + \Lambda^- = \sigma^+/C^+ + \sigma^-/C^-$$

$$t_j = \frac{I_j}{I} = \frac{I_j^+}{I} + \frac{I_j^-}{I} = \frac{|Z_j| e \cdot n_j v_j}{\sum |Z_j| e \cdot n_j v_j} = \frac{|Z_j| e \cdot n_j \mu_j}{\sum |Z_j| e \cdot n_j \mu_j}$$

Ionic conductivity (σ)

Grotthuss mechanism

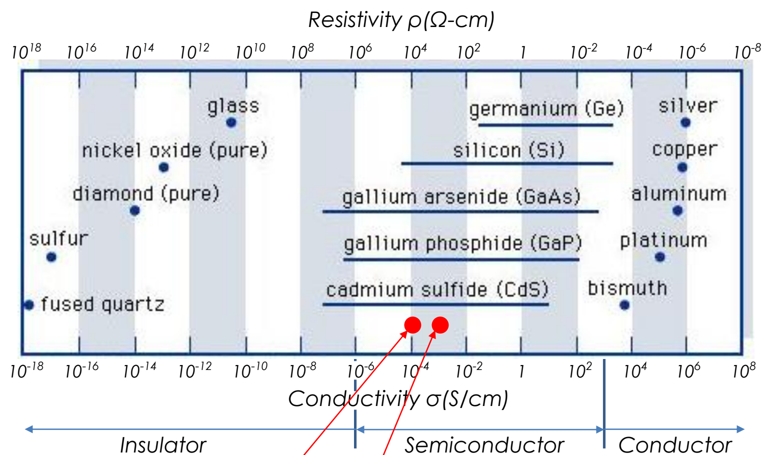
表 9－2　モルイオン伝導率と移動度(25℃)

イオン	$\lambda_+/10^{-4}$ S・m²・mol⁻¹	$u_+/10^{-8}$ m²・s⁻¹・V⁻¹	イオン	$\lambda_-/10^{-4}$ S・m²・mol⁻¹	$u_-/10^{-8}$ m²・s⁻¹・V⁻¹
H^+	349.82	36.3	OH^-	198.0	20.5
Li^+	38.69	4.01	Cl^-	75.23	7.91
Na^+	50.11	5.19	Br^-	78.4	8.01
K^+	73.52	7.61	I^-	76.8	7.95
Ag^+	61.92	6.41	NO_3^-	71.44	7.40
NH_4^+	73.4	7.60	HCO_3^-	44.5	4.61
Ca^{2+}	59.50	6.16	CH_3COO^-	40.9	4.23
Mg^{2+}	53.06	5.50	SO_4^{2-}	79.8	8.27

$$\Lambda^\infty = \nu_+ \lambda_+^{\ \infty} + \nu_- \lambda_-^{\ \infty}$$

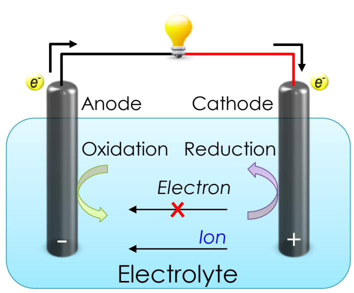
Where ν_+ and ν_- are the number of cations and anions per formula unit of electrolyte respectively, λ_+^∞ and λ_-^∞ are the molar conductivities of the cation and anion at infinite dilution respectively.

Conductivity (σ)



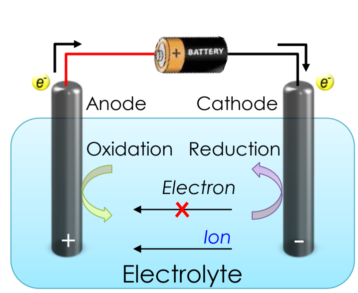
Proton (H^+): 10^{-3} S cm^{-1}

Sodium ion (Na^+): 10^{-4} S cm^{-1}



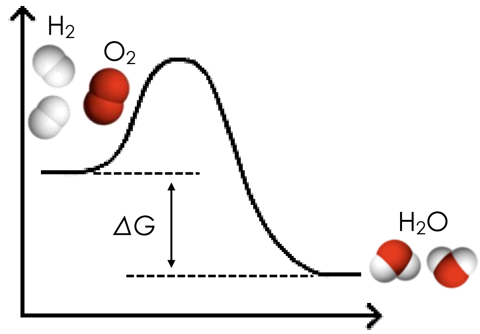
Galvanic cell

$$V \cong IR$$



Electronic cell

External circuits(Electron) Electrolyte(Ion conductivity) Electrode(Ion)	**Resistance**	External circuits(Electron) Electrolyte(Ion conductivity) Electrode(Ion)
	Voltage	Power supply Electrochemical potential (in battery)
	Current	Faradaic or non-faradaic reaction



Chemical reaction

$$A \leftrightarrow B$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

Electrochemical reaction

$$O_X + ne^- \leftrightarrow R_{ed}$$

Oxidized form Reduced form

$$2H_2 \rightarrow 4H^+ + 4e^-$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Chemical reaction

$$A \leftrightarrow B$$

A B

Neutral

Electrochemical reaction

$$O_X + ne^- \leftrightarrow R_{ed}$$

O_X^{3+} R_{ed}^{2+}

Chemical potential

$$\mu_i = \mu_i^\circ + RT\ln a_i$$

a_i: *activity of the species*

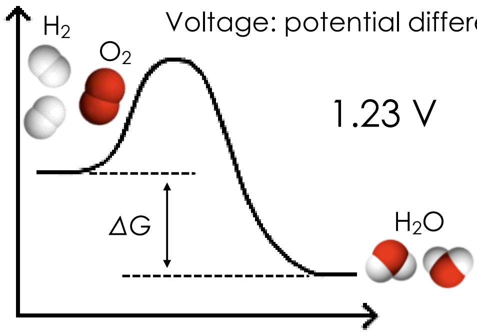
Electrochemical potential

$$\tilde{\mu}_i = \mu^\circ{}_i + RT\ln a_i + \quad (Eq\ 3.2)$$

$$\tilde{\mu}_i = \mu_i + \quad (Eq\ 3.3)$$

$\emptyset$: *electric potential*
Z_iF: *the charge of one mole of ions*

The electrochemical potential was introduced by *Guggenheim*.
The potential $\tilde{\mu}_i$ is the sum of the chemical potential μ_i and the electric potential $z_iF\emptyset$.



$$2H_2 + O_2 \rightarrow 2H_2O$$

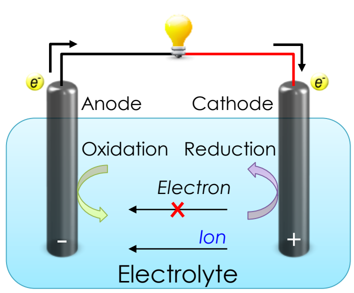
$$H_2 \rightarrow 2H^+ + 2e^-$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Glucose-O_2: 1.25V

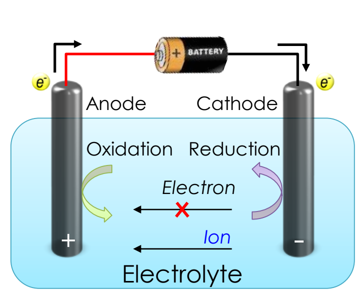
E° vs. SHE

				$E^{\circ\prime}$/V
1	$O_2 + 4H^+ + 4e^-$	↔	$2H_2O$	+0.82
2	$2HNO_3 + 10H^+ + 10e^-$	↔	$N_2 + 6H_2O$	+0.80
3	$CO_2 + 8H^+ + 8e^-$	↔	CH_4（メタン）$+ 2H_2O$	−0.25
4	$NAD^+ + H^+ + 2e^-$	↔	NADH	−0.32
5	HCOOH（蟻酸）$+ 4H^+ + 4e^-$	↔	CH_3OH（メタノール）$+ H_2O$	−0.36
6	グルコン酸 $+ 2H^+ + 2e^-$	↔	グルコース（ブドウ糖）$+ H_2O$	−0.36
7	$CO_2 + 6H^+ + 6e^-$	↔	CH_3OH（メタノール）$+ H_2O$	−0.40
8	CH_3COOH（酢酸）$+ 4H^+ + 4e^-$	↔	CH_3OH（エタノール）$+ H_2O$	−0.40
9	$2H^+ + 2e^-$	↔	H_2	−0.41
10	$6CO_2 + 24H^+ + 24e^-$	↔	グルコース（ブドウ糖）$+ 6H_2O$	−0.43
11	$2CO_2 + 12H^+ + 12e^-$	↔	C_2H_5OH（エタノール）$+ 3H_2O$	−0.50



Galvanic cell

$$V \cong IR$$

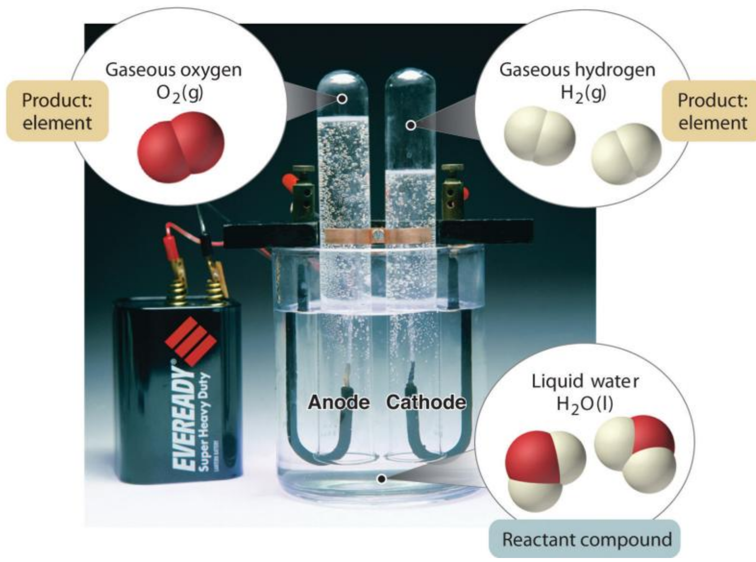


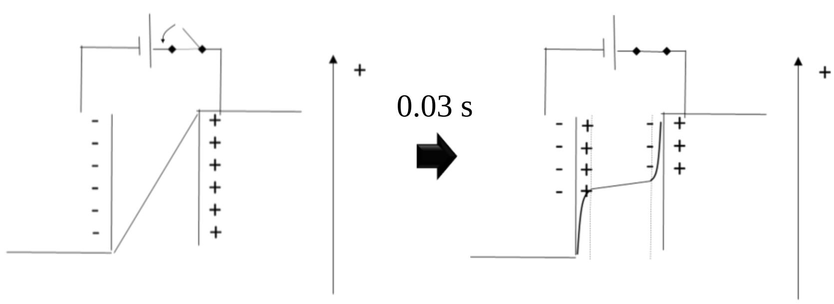
Electronic cell

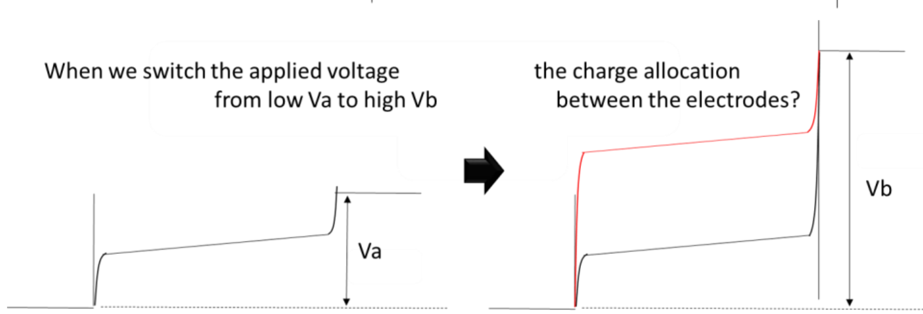
External circuits(Electron) Electrolyte(Ion conductivity) Electrode(Ion)	**Resistance**	External circuits(Electron) Electrolyte(Ion conductivity) Electrode(Ion)
	Voltage	Power supply Electrochemical potential (in battery)
	Current	Faradaic or non-faradaic reaction

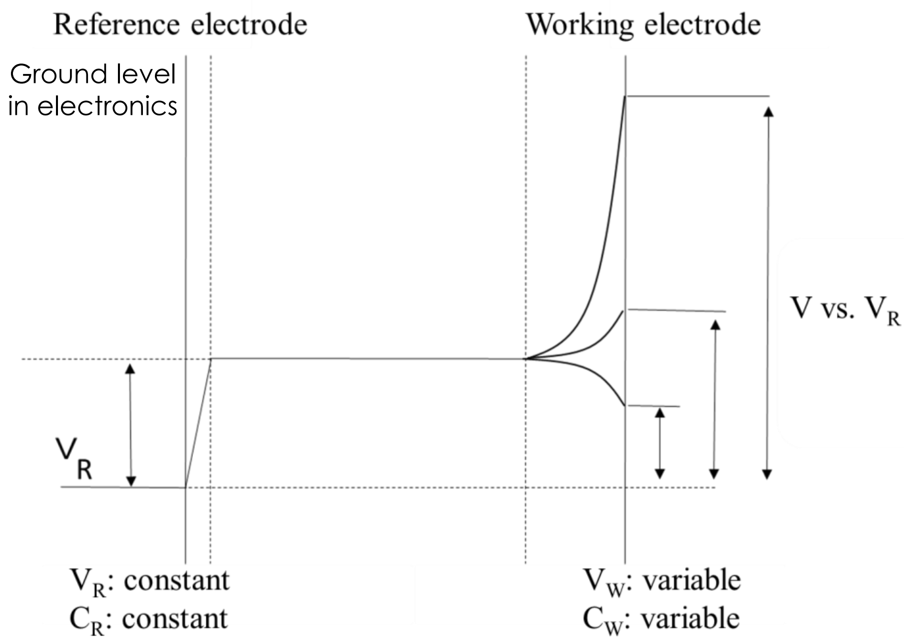
Electrolysis of water

$$2H_2O \rightarrow 2H_2 + O_2$$





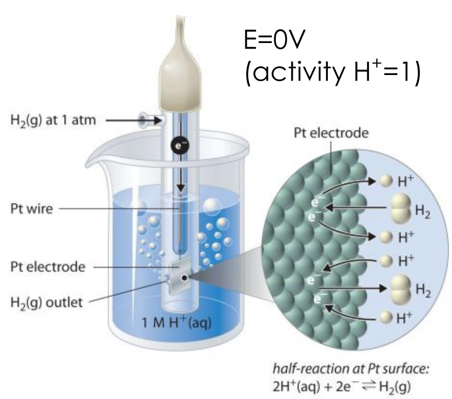




Reference electrode(参照電極)

Standard hydrogen electrode

E=0V
(activity H^+=1)

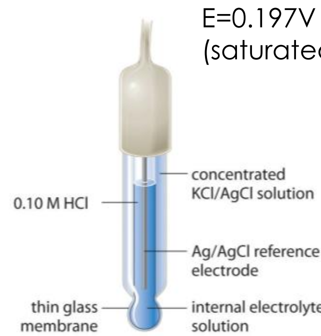


$$2H^+(aq) + 2e^- \rightleftarrows H_s(g)$$

$$E = E^0 + \frac{RT}{F} ln \frac{a_{H+}}{(p_{H2}/p^0)^{1/2}}$$

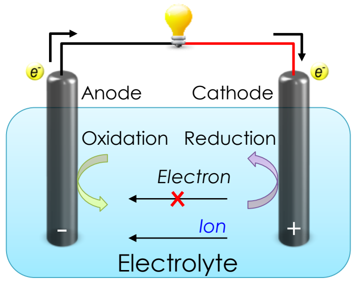
Ag/AgCl electrode

E=0.197V
(saturated)



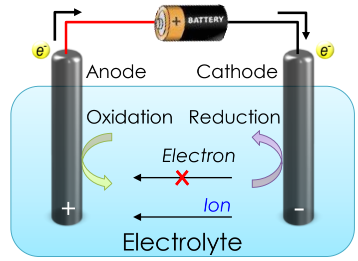
$$AgCl + e^- \rightleftarrows Ag + Cl^-$$

$$E = E^0 + \frac{RT}{F} lna_{Cl^-}$$



Galvanic cell

$$V \cong IR$$

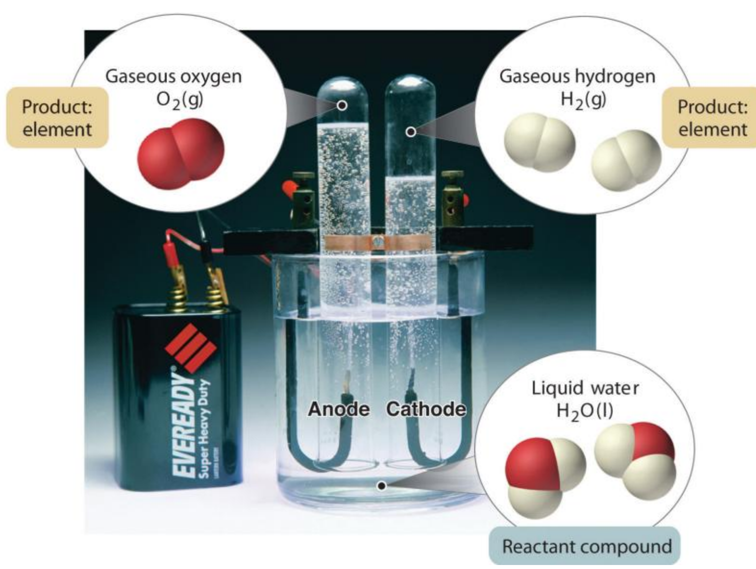


Electronic cell

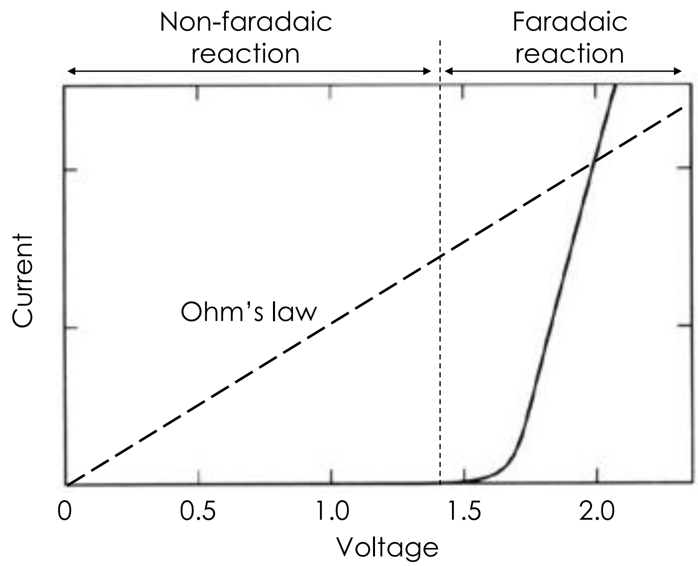
Galvanic cell		Electronic cell
External circuits(Electron) Electrolyte(Ion conductivity) Electrode(Ion)	**Resistance**	External circuits(Electron) Electrolyte(Ion conductivity) Electrode(Ion)
Electrochemical potential	**Voltage**	Power supply Electrochemical potential (in battery)
	Current	Faradaic or non-faradaic reaction

Electrolysis of water

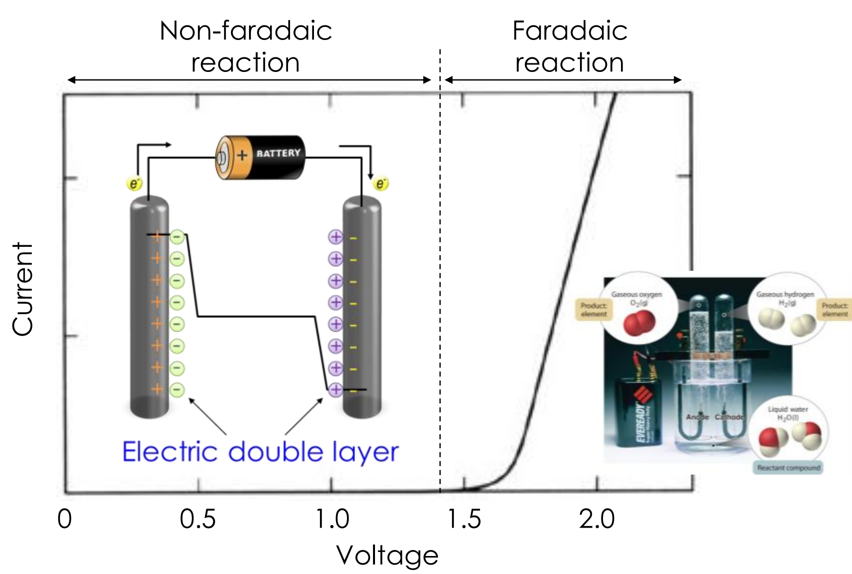
$$2H_2O \rightarrow 2H_2 + O_2$$



Electrolysis of water

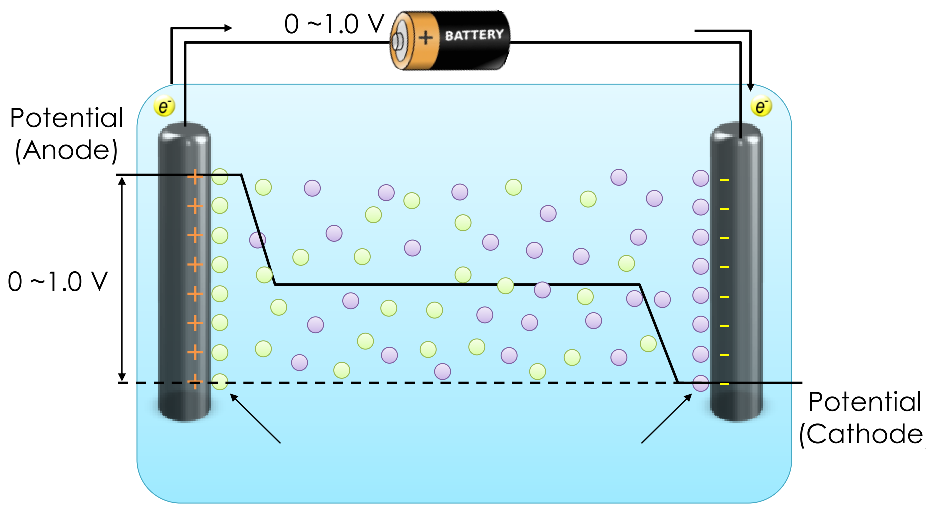


Electrolysis of water



Non-faradic reaction

Potential and ions distribution
away from a charged surface



The Helmholtz model

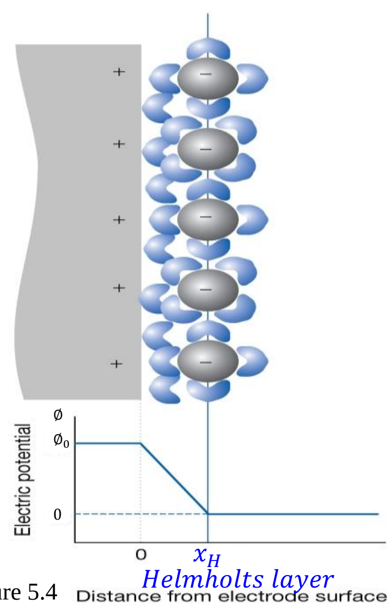


Figure 5.4

Gibbs-Helmholtz equation

Young-Helmholtz theory

Helmholtz-Thevenin's theorem

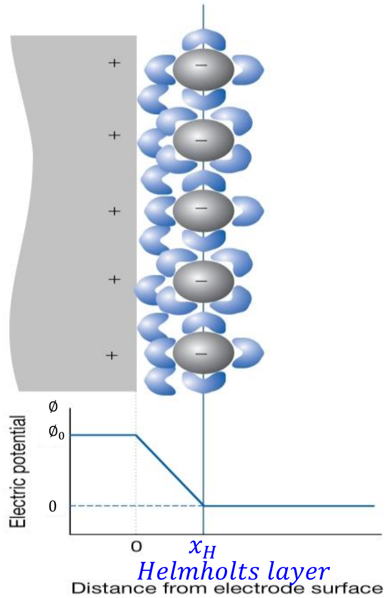
Helmholtz coil

Hermann Ludwig Ferdinand von Helmholtz

$$Ø = Ø_0\left(1 - \frac{1}{x_H}X\right) \qquad (Eq\ 5.3)$$

Linear potential drop from the surface to the Helmholtz layer (x_H)

The Helmholtz model



Gibbs-Helmholtz equation

Young-Helmholtz theory

Helmholtz-Thevenin's theorem

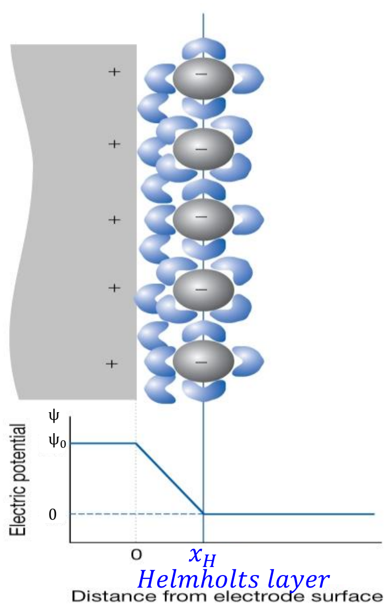
Helmholtz coil

Hermann Ludwig Ferdinand von Helmholtz

$$\frac{C_H}{A} = \frac{dq}{dE} = \frac{\varepsilon_H}{x_H} \quad \text{Helmholtz model} \quad (Eq\ 5.4)$$

Where ε_H is the Helmholts permittivity, but the precise significance that attaches to each of these quantities separately is open to interpretation.

The Helmholtz model



Gibbs-Helmholtz equation

Young-Helmholtz theory

Helmholtz-Thevenin's theorem

Helmholtz coil

Hermann Ludwig Ferdinand von Helmholtz

$$\frac{C_H}{A} = \frac{dq}{dE} = \frac{\varepsilon_H}{x_H} \quad (Eq\ 5.4)$$

Does not take into account

- Thermal motion
- Ion diffusion
- Adsorption on the surface
- Solvent/surface interaction

The Gouy-Chapman model

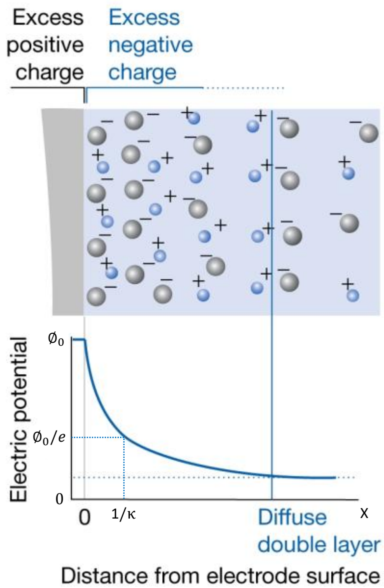


Figure 5.5

$$\emptyset = \emptyset_0 e^{-\kappa X} \qquad (Eq\ 5.5)$$

Exponential potential decrease

The ions are mobile in the electrolyte
(diffusion, electrostatic forces)

Boltzmann statistical distribution

Debye length (1/κ): "thickness of diffuse double layer"

Account

- Thermal motion
- Ion diffusion

The Sterm model

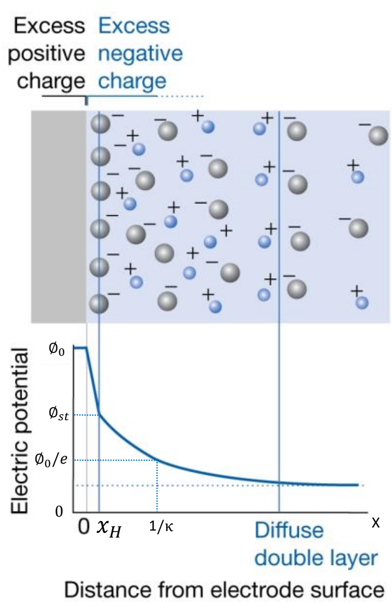


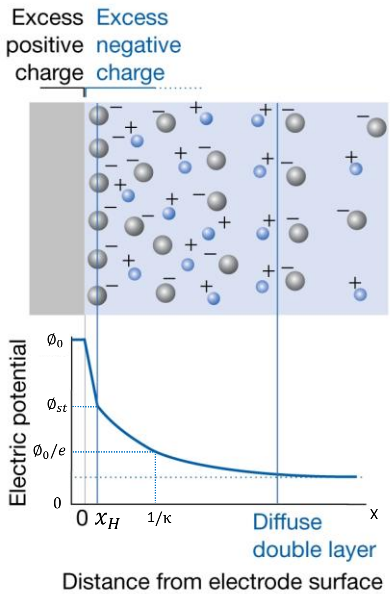
Figure 5.7

Stern recognized that the experimental capacitance results were better matched by a melding of the Helmholtz and Gouy-Chapman models, some of the counterions being in a diffuse zone and some in a compact layer immediately adjacent to the interface.

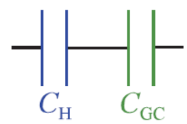
$$\emptyset = \emptyset_0 \left(1 - \frac{1}{x_H} X\right) \qquad (Eq\ 5.12)$$

$$\emptyset = \emptyset_{St} e^{-\kappa(X - x_H)} \qquad (Eq\ 5.13)$$

The Sterm model



Capacitances arising from the two regions would be in series and so the overall capacitance would be calculable from the formula

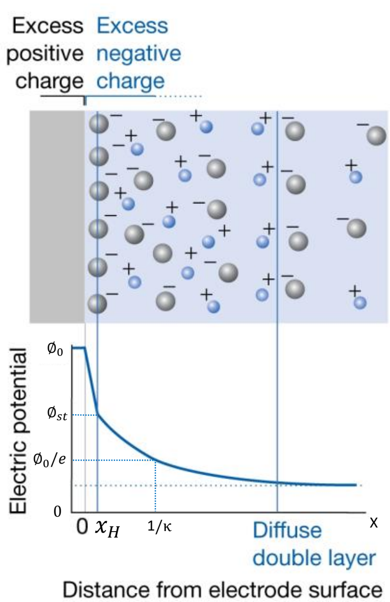


$$\frac{1}{C_s} = \frac{1}{C_H} + \frac{1}{C_{GC}}$$

$$= \frac{x_H}{A\varepsilon_H} + \frac{\sqrt{RT/2F^2\varepsilon c}}{A\cosh\{F(E - E_{ZC})/RT\}}$$

Stern model (*Eq* 5.14)

The Sterm model



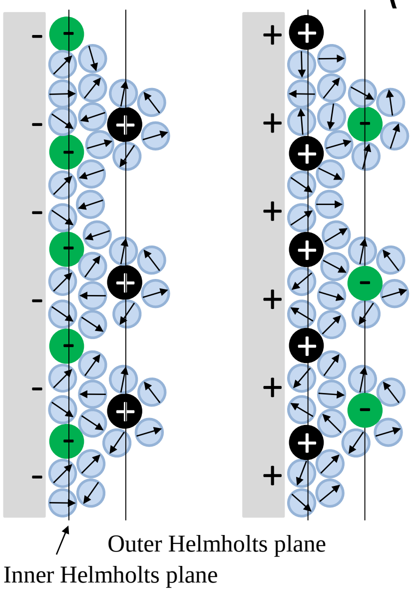
The permittivity enters equation 5.14 twice, but its significance differs between the two instances. The permittivity ε in the disordered diffuse zone will be close to that of pure water, about $79\varepsilon_0$. However, the permittivity ε_H in the compact layer is that of water-plus-ions confined in a narrow region, compressed, and ordered by an intense local field; estimates suggest that the permittivity here is much lower, perhaps as small as $5\varepsilon_0$.

$$\frac{1}{C_s} = \frac{1}{C_H} + \frac{1}{C_{GC}}$$

$$= \frac{x_H}{A\varepsilon_H} + \frac{\sqrt{RT/2F^2\varepsilon c}}{A\cosh\{F(E - E_{ZC})/RT\}}$$

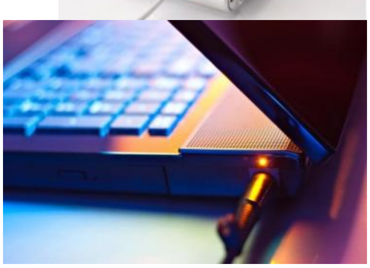
Stern model (*Eq* 5.14)

Bockris-Devanathan-Müller(BDM)model

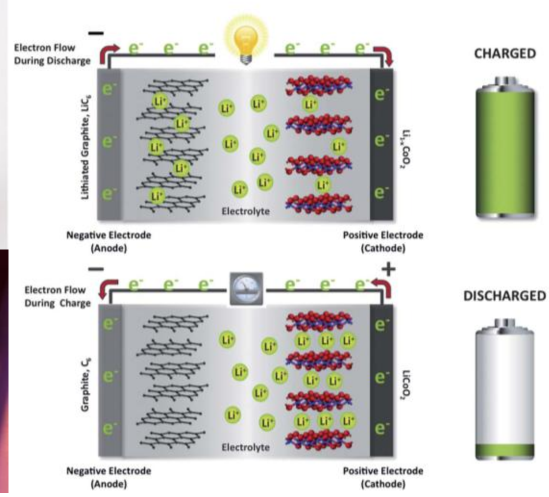


In 1963 J. O'M. Bockris, M. A. V. Devanathan and Klaus Müller proposed the BDM model of the double-layer that included the action of the solvent in the interface. They suggested that the attached molecules of the solvent, such as water, would have a fixed alignment to the electrode surface. This first layer of solvent molecules displays a strong orientation to the electric field depending on the charge. This orientation has great influence on the permittivity of the solvent that varies with field strength. The inner Helmholtz plane (IHP) passes through the centers of these molecules. Specifically adsorbed, partially solvated ions appear in this layer. The solvated ions of the electrolyte are outside the IHP. Through the centers of these ions pass the outer Helmholtz plane (OHP). The diffuse layer is the region beyond the OHP. **The BDM model is currently the most commonly used.**

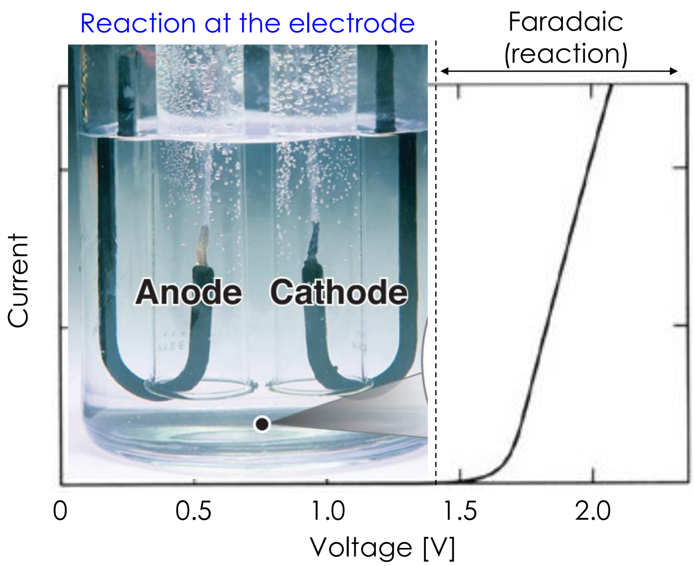
Application of double layer



Lithium-ion rechargeable battery



Electrolysis of water



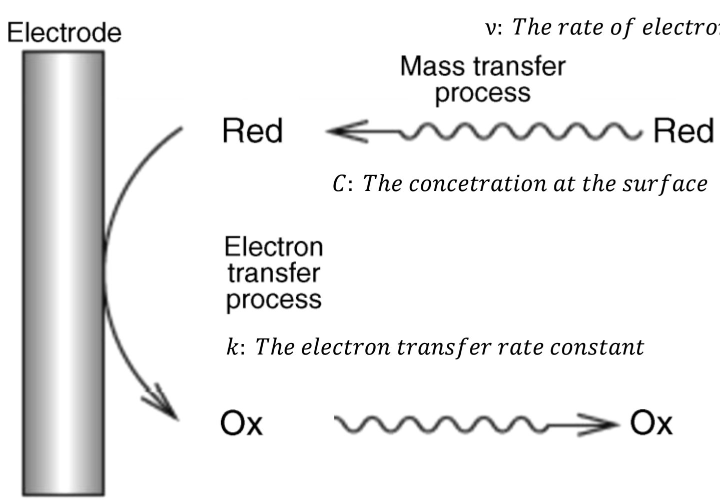
Reaction at the electrode

$$O_X + ne^- \underset{\nu_{R_{ed}}}{\overset{\nu_{O_x}}{\rightleftarrows}} R_{ed}$$

$$\nu_{O_x} = k_{O_x} C_{O_x}(0,t)$$

$$\nu_{R_{ed}} = k_{R_{ed}} C_{R_{ed}}(0,t)$$

ν: *The rate of electron transfer*



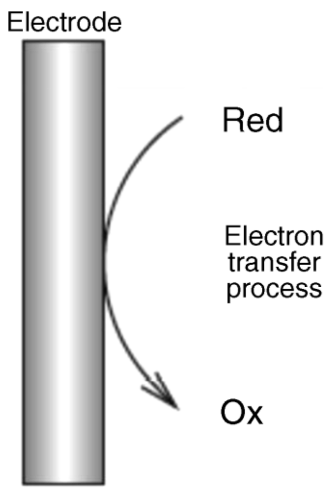
Kinetic current

$$O_X + ne^- \underset{\nu_{Red}}{\overset{\nu_{O_x}}{\rightleftarrows}} R_{ed}$$

$$\nu_{O_x} = k_{O_x} C_{O_x}(0,t)$$

$$\nu_{Red} = k_{Red} C_{Red}(0,t)$$

ν: $The\ rate\ of\ electron\ transfer$



Butler-Volmer equation

$$I = -nF(\nu_{Ox} - \nu_{Red})$$

$$= -nFk^0\left(C_{O_x}(0,t)exp(-\alpha nF(E-E^0)/RT)\right) - \left(C_{Red}(0,t)exp((1-\alpha)nF(E-E^0)/RT)\right)$$

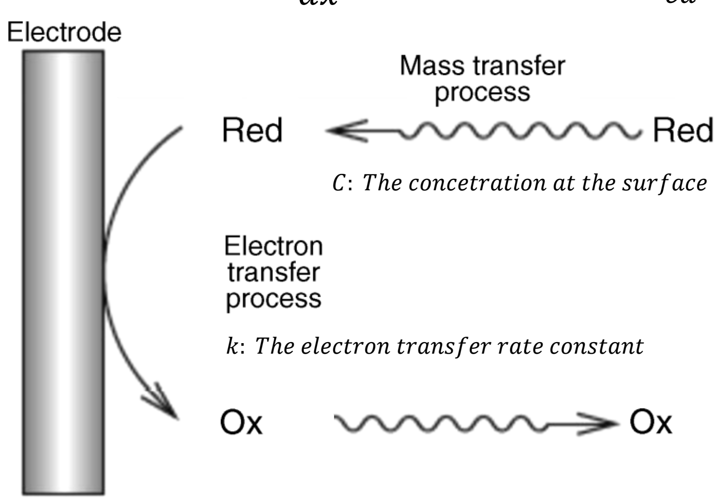
$$k_{ox} = k^0 exp(-\alpha nF(E-E^0)/RT)$$

$$k_{Red} = k^0 exp((1-\alpha)nF(E-E^0)/RT)$$

Diffusion-limited current

Fick's first law

$$J_i = -D_i \frac{dC_i}{dx} \quad \longrightarrow \quad I_a = nFD_{Red}\frac{dC_{Red}}{dx}$$



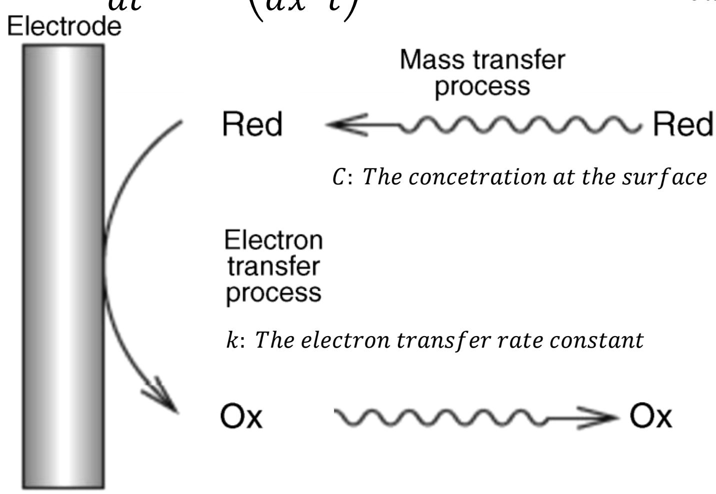
Diffusion-limited current

Fick's second law

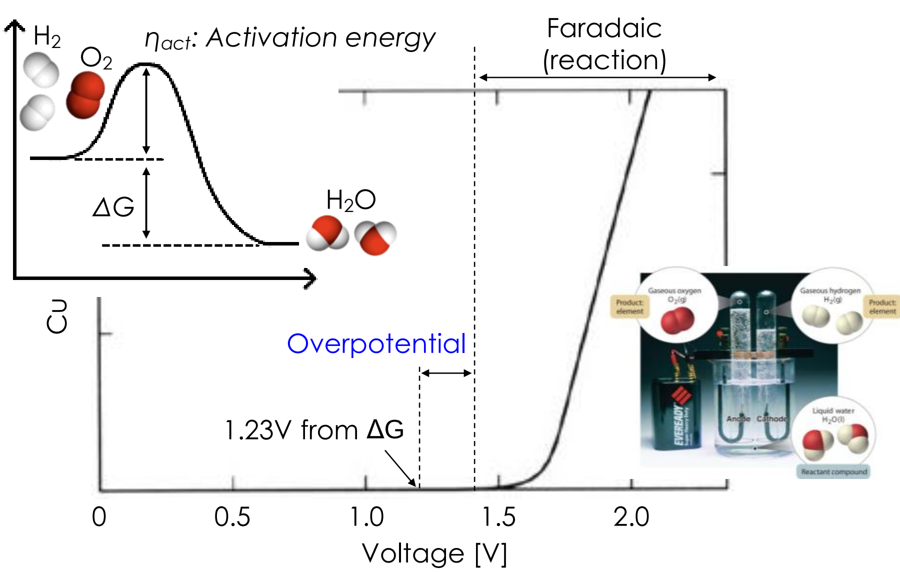
$$\frac{dC_i}{dt} = D_i\left(\frac{d^2C_i}{dx^2t}\right) \longrightarrow$$

Cottrell equation

$$I_a = nFC_{Red}\sqrt{\left(\frac{D_{Red}}{\pi t}\right)}$$



Electrolysis of water



Analysis of electrode reaction

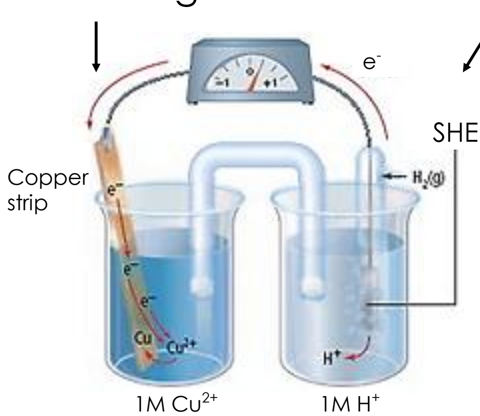
- Oxidation reduction potential (ORP)
  Open circuit potential (OCP)

- Potential step voltammetry
  Linear sweep voltammetry
  Cyclic voltammetry

- AC impedance measurement

Oxidation reduction potential (ORP)
Open circuit potential (OCP)

Working electrode　　　Reference electrode



Standard hydrogen electrode (SHE)

Ag/AgCl electrode

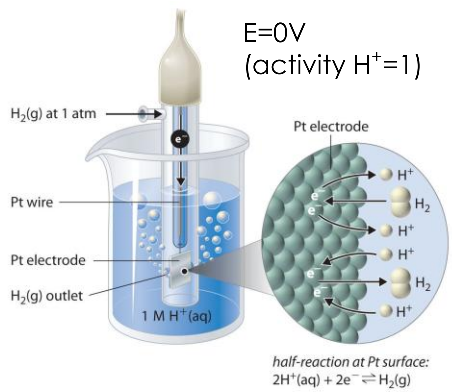
Reversible hydrogen electrode (RHE)

Saturated calomel electrode (SCE)

Reference electrode(参照電極)

Standard hydrogen electrode

E=0V
(activity H^+=1)

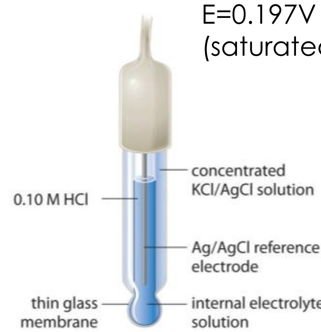


$$2H^+(aq) + 2e^- \rightleftarrows H_s(g)$$

$$E = E^0 + \frac{RT}{F} ln \frac{a_{H+}}{(p_{H2}/p^0)^{1/2}}$$

Ag/AgCl electrode

E=0.197V
(saturated)



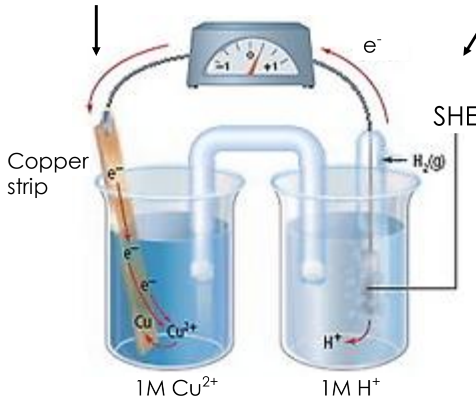
$$AgCl + e^- \rightleftarrows Ag + Cl^-$$

$$E = E^0 + \frac{RT}{F} lna_{Cl^-}$$

Oxidation reduction potential (ORP)
Open circuit potential (OCP)

Working electrode

Reference electrode



Constant potential

Standard hydrogen electrode (SHE)

Ag/AgCl electrode

Reversible hydrogen electrode (RHE)

Saturated calomel electrode (SCE)

Analysis of electrode reaction

- Oxidation reduction potential (ORP)
  Open circuit potential (OCP)

- Potential step voltammetry
  Linear sweep voltammetry
  Cyclic voltammetry

- AC impedance measurement

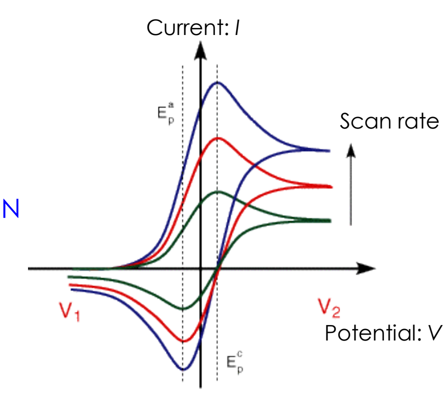
Voltammetry

Analysis of electrochemical reaction
at the Working Electrode **(WE)**

POTENTIAL ⇔ CURRENT

POTENTIAL ⇔ CONCENTRATION

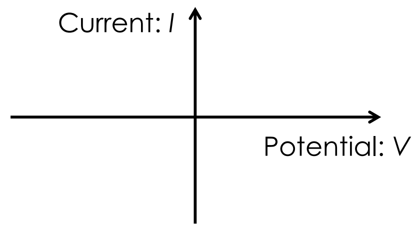
SCAN RATE ⇔ CURRENT

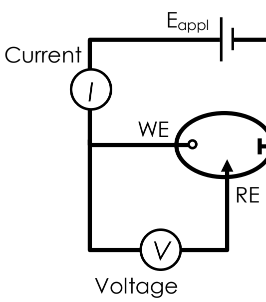


Voltammetry

Measurement of current as a function of potential applied by a potentiostat (a three-electrode system)

WE: Working electrode
RE: Reference electrode
CE: Counter electrode

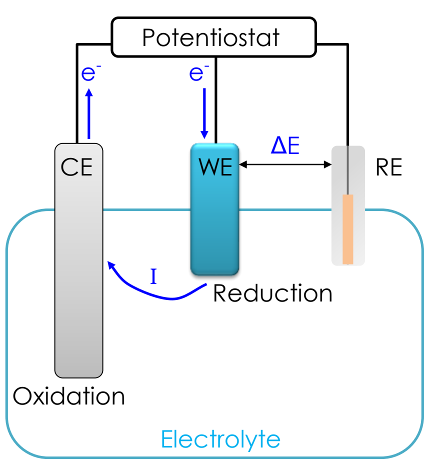




Three-electrode *system*

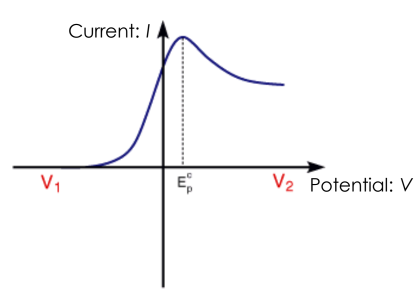
Potentiostat

Potentiostat system



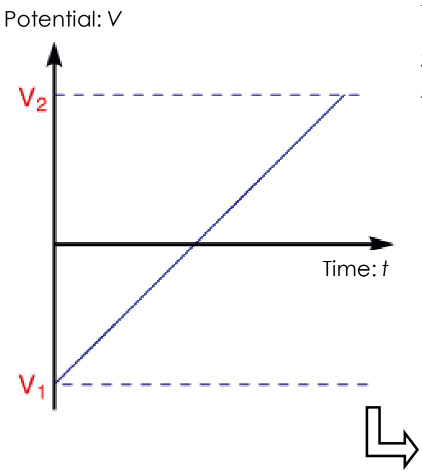
The system basically maintains the POTENTIAL(ΔE) of the **WE** at a constant level with respect to the **RE** by adjusting the CURRENT (I) at the **CE**

Analysis of electrochemical reaction at the **WE**



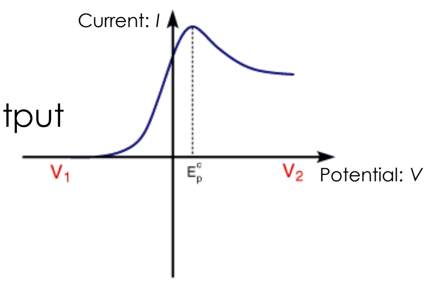
Linear sweep voltammetry

Input



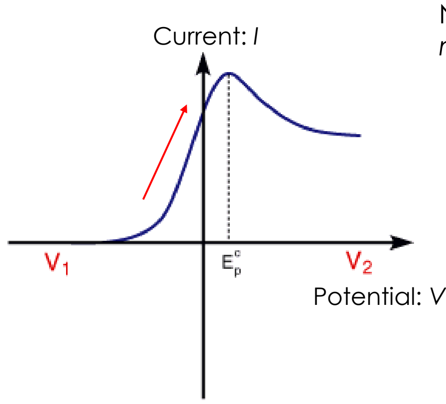
1. A fixed potential range.
2. Voltage is changed (scanned) from a V_1 to V_2 over time.
3. Voltage scan rate = slope of line
4. Characteristics of voltammogram depends on
   - Rate of electron transfer
   - Chemical reactivity
   - Voltage scan rate

Output



POTENTIAL ⇔ CURRENT

Linear sweep voltammetry

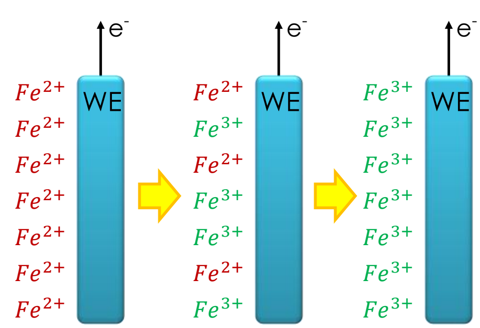


Note:
no stirring

Reduction

$$Fe^{3+} + e^{-} \rightleftarrows Fe^{2+}$$

Oxidation



Nernst equation

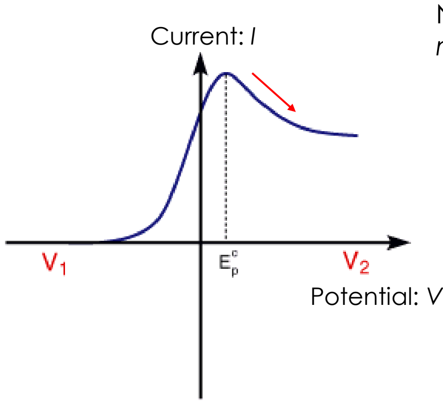
$$E = E^0 + \frac{RT}{nF} ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

POTENTIAL ⇔ CONCENTRATION

Current increase from V_1 to E_p^0

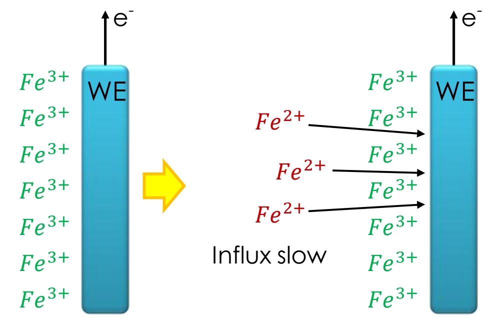
Rate of electron transfer is fast vs voltage sweep

Linear sweep voltammetry



Note:
no stirring

Reduction
$$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$$
Oxidation



Nernst equation

$$E = E^0 + \frac{RT}{nF} ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

POTENTIAL ⇔ CONCENTRATION

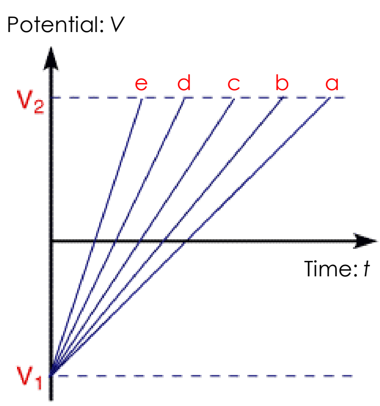
Current drops from E_p^0

Influx of Fe^{2+} not fast enough to satisfy the Nernst equation

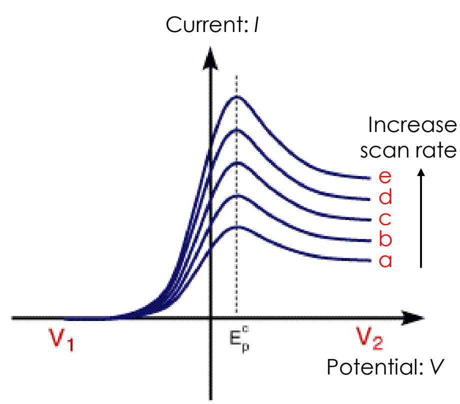
Diffusion-limited current

Linear sweep voltammetry

Input



Output



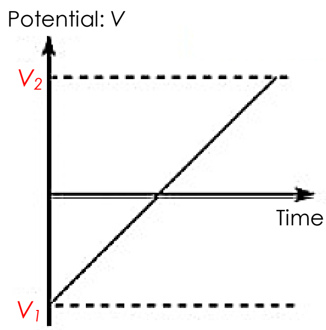
SCAN RATE ⇔ CURRENT

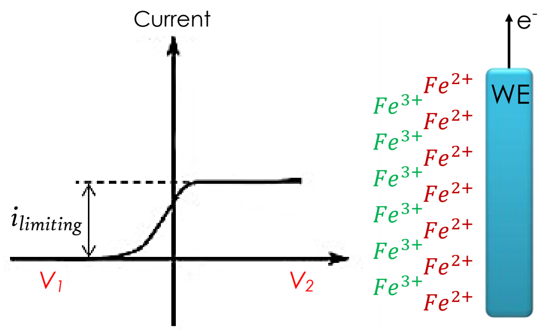
- Each curve: same form
- *Total current increases with increasing scan rate*
- *Position of the current maximum remains the same potential*

Linear sweep voltammetry

Note:
With stirring

Steady state conditions:
The influx of Fe^{2+} does not change in time.





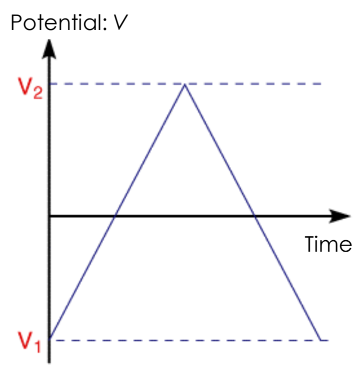
- No peak
- $i_{limiting} \propto [Fe^{2+}]$
- $i_{limiting}$ is constant

Kinetic current

Fe^{2+} constantly replaced by ready influx from bulk solution.

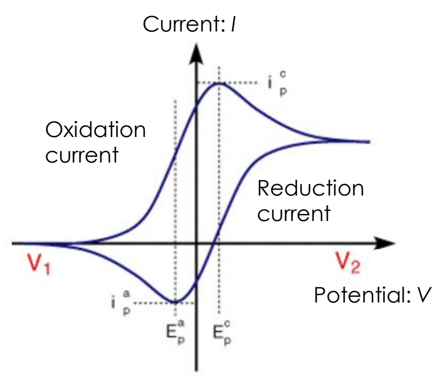
Cyclic voltammetry

Input



Scan is reversed when voltage reaches one end.

Output

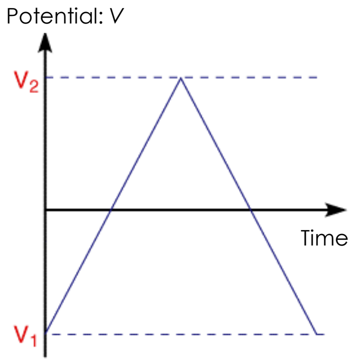


Forward scan: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

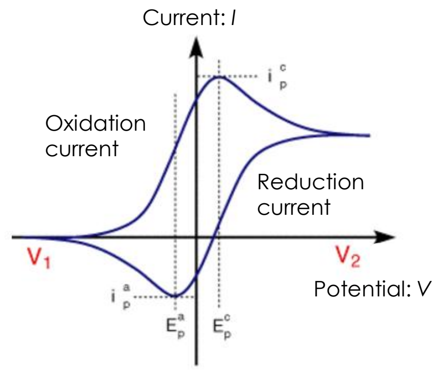
Reversed scan: $Fe^{3+} + e^- \rightarrow Fe^{2+}$

Cyclic voltammetry

Input



Output



$$E_{midpoint} = \frac{(E_p{}^a + Epc)}{2} = E^0 + \frac{RT}{nF} ln \frac{[D_R{}^{1/2}]}{[D_O{}^{1/2}]}$$

Same value when the pH is changed by 1.0 pH.

$$\Delta E_p = |E_p{}^a - E_p{}^c| = 2.3\frac{RT}{nF} = \frac{59}{n} mV\ (at\ 289K)$$

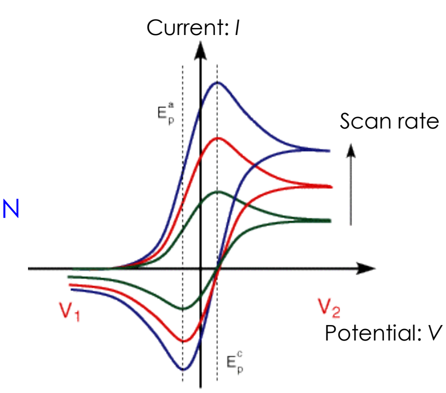
Cyclic voltammetry

Analysis of electrochemical reaction at the Working Electrode **(WE)**

POTENTIAL ⟺ CURRENT

POTENTIAL ⟺ CONCENTRATION

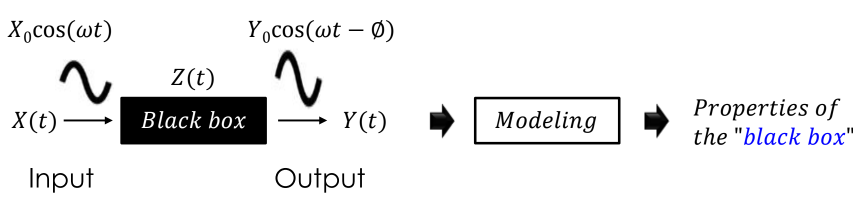
SCAN RATE ⟺ CURRENT

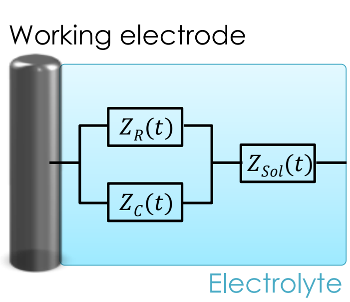


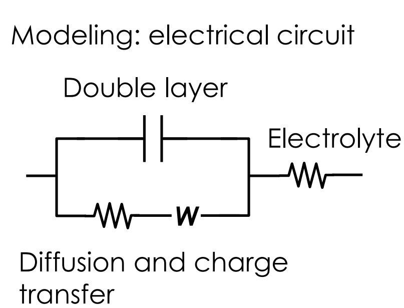
Analysis of electrode reaction

- Oxidation reduction potential (ORP)
  Open circuit potential (OCP)
- Potential step voltammetry
  Linear sweep voltammetry
  Cyclic voltammetry
- AC impedance measurement

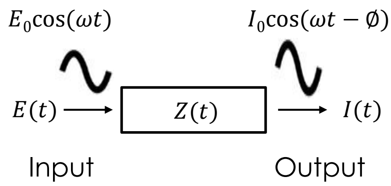
AC impedance system







AC impedance system

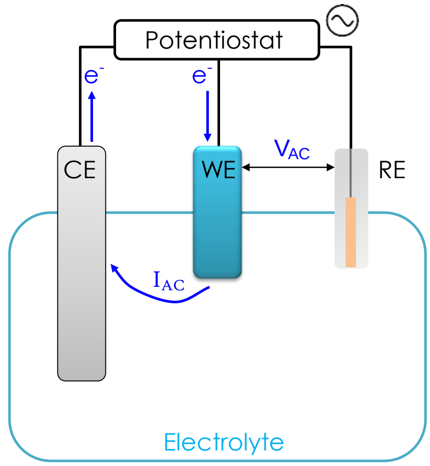


Transfer function（伝達関数）

Resistance

$$Z(t) = \frac{E(t)}{I(t)} = \frac{E_0\cos(\omega t)}{I_0\cos(\omega t - \emptyset)}$$

$$= Z_0\frac{\cos(\omega t)}{\cos(\omega t - \emptyset)}$$



Transfer function
（伝達関数）

$$G(t) = \frac{Y(t)}{X(t)}$$

Laplace transform
$(t \rightarrow s = j\omega)$

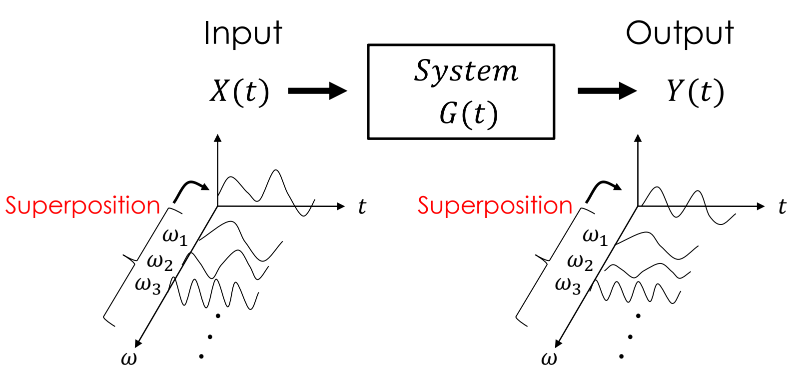
$$G(s) = \frac{Y(s)}{X(s)}$$

⇔

Frequency
transfer function
（周波数伝達関数）

$$G(jw) = \frac{Y(jw)}{X(jw)} = \alpha + j\beta$$

j: *imaginary unit*



Transfer function
（伝達関数）

$$G(t) = \frac{Y(t)}{X(t)}$$

Laplace transform
$(t \to s = j\omega)$

$$G(s) = \frac{Y(s)}{X(s)}$$

⇔

Frequency
transfer function
（周波数伝達関数）

$$G(jw) = \frac{Y(jw)}{X(jw)} = \alpha + j\beta$$

j: *imaginary unit*

Resistor

$$I = \frac{V}{R}$$

Impedance

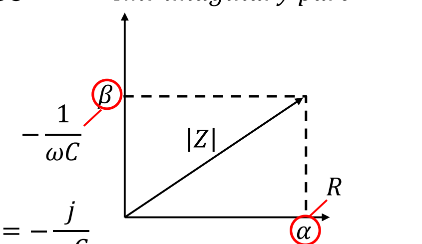
$$Z_R = R$$

Capacitor

$$I = C\frac{dV}{dt}$$

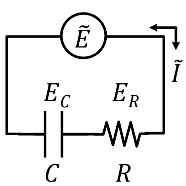
$$Z_c = \frac{1}{j\omega C} = -\frac{j}{\omega C}$$

Im: *imaginary part*



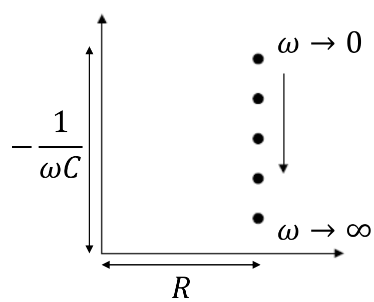
Re: *real part*

Series R-C circuit

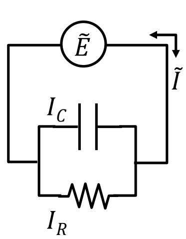


$$\tilde{E} = EC + ER$$

$$Z = R - \frac{1}{\omega C}j$$

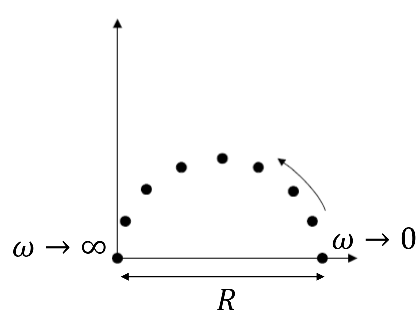


Parallel R-C circuit

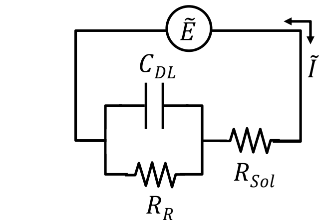


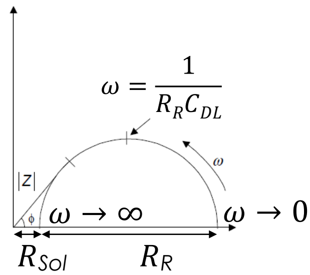
$$\tilde{I} = IC + IR$$

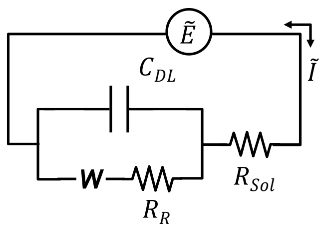
$$Z = \frac{1}{R} + \omega Cj$$

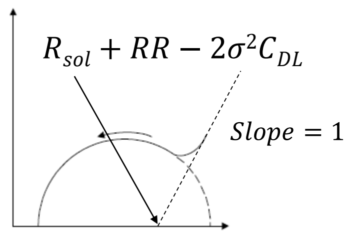


Combining impedances in series and parallel



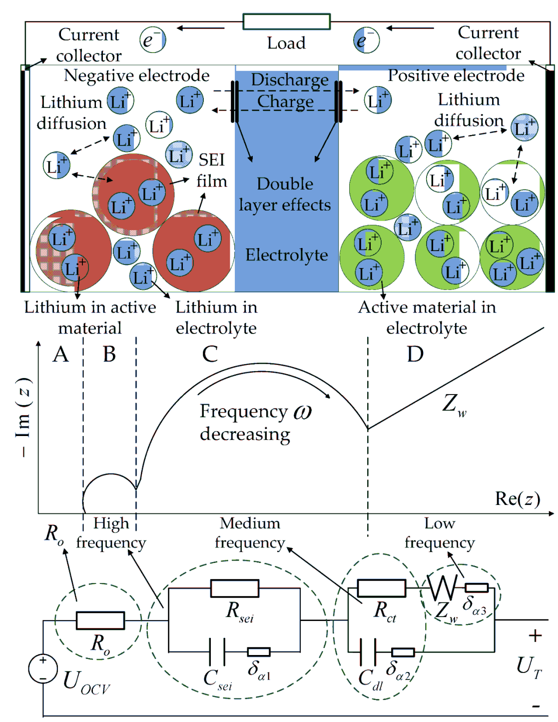






Warburg diffusion element

$$Z_W = \sigma(1 - j)/\sqrt{\omega} \qquad \sigma = \frac{RT}{\sqrt{2}n^2AF^2}\left[\frac{1}{\sqrt{D_0}C_0} + \frac{1}{\sqrt{D_R}C_R}\right]$$



Energies **2016**, *9*(3), 123; doi:10.3390/en9030123