

Electrochemical Engineering

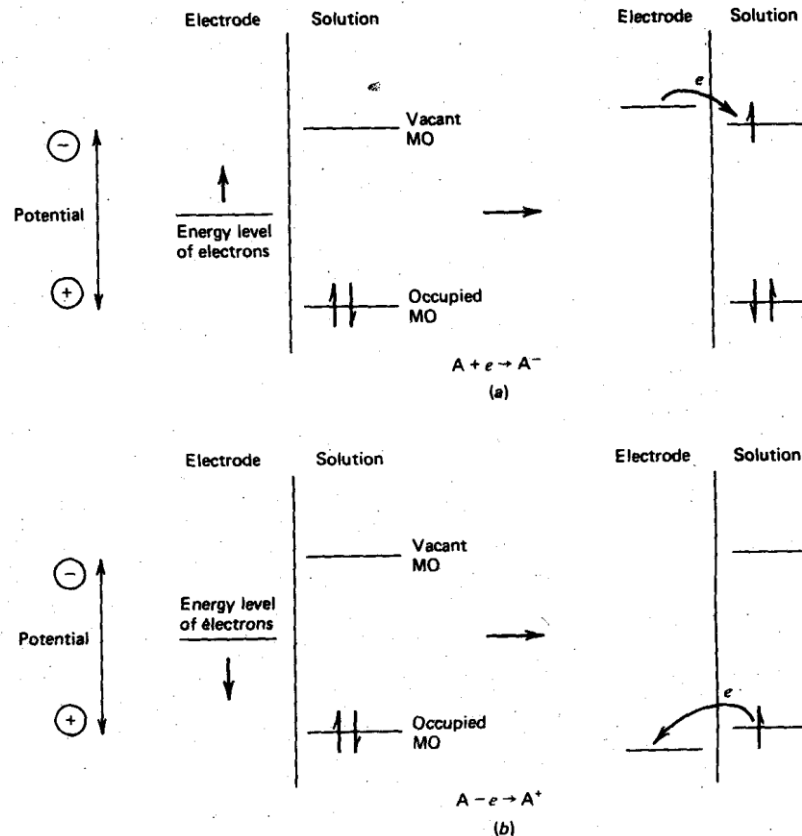
Chapter 2 - Thermodynamics

Bing Joe Hwang

NTUST

Definition of Electrochemistry

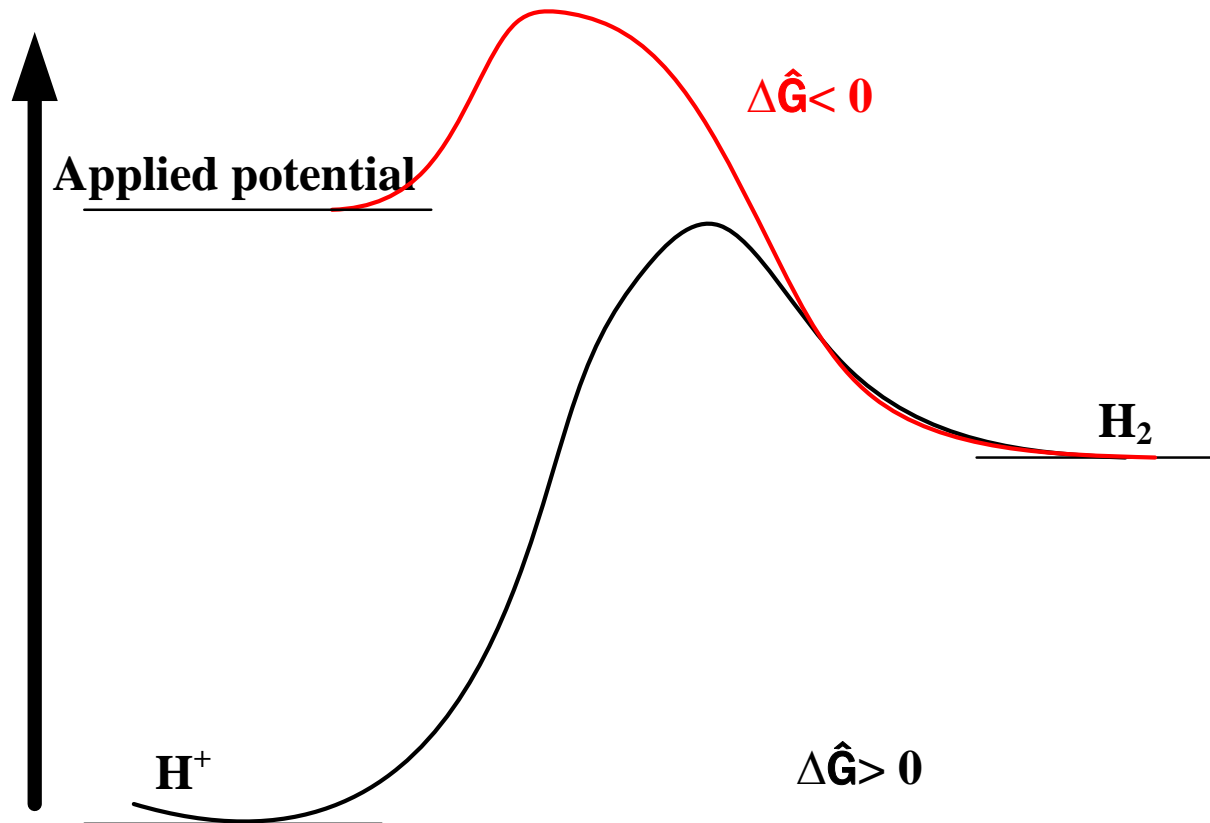
Electrochemical Reactions: Reactions involve the charge transfer (usually electron) across an interface between two phases (e.g., a **solid** and an adjacent **solution**).



Gibbs Free Energy (ΔG)

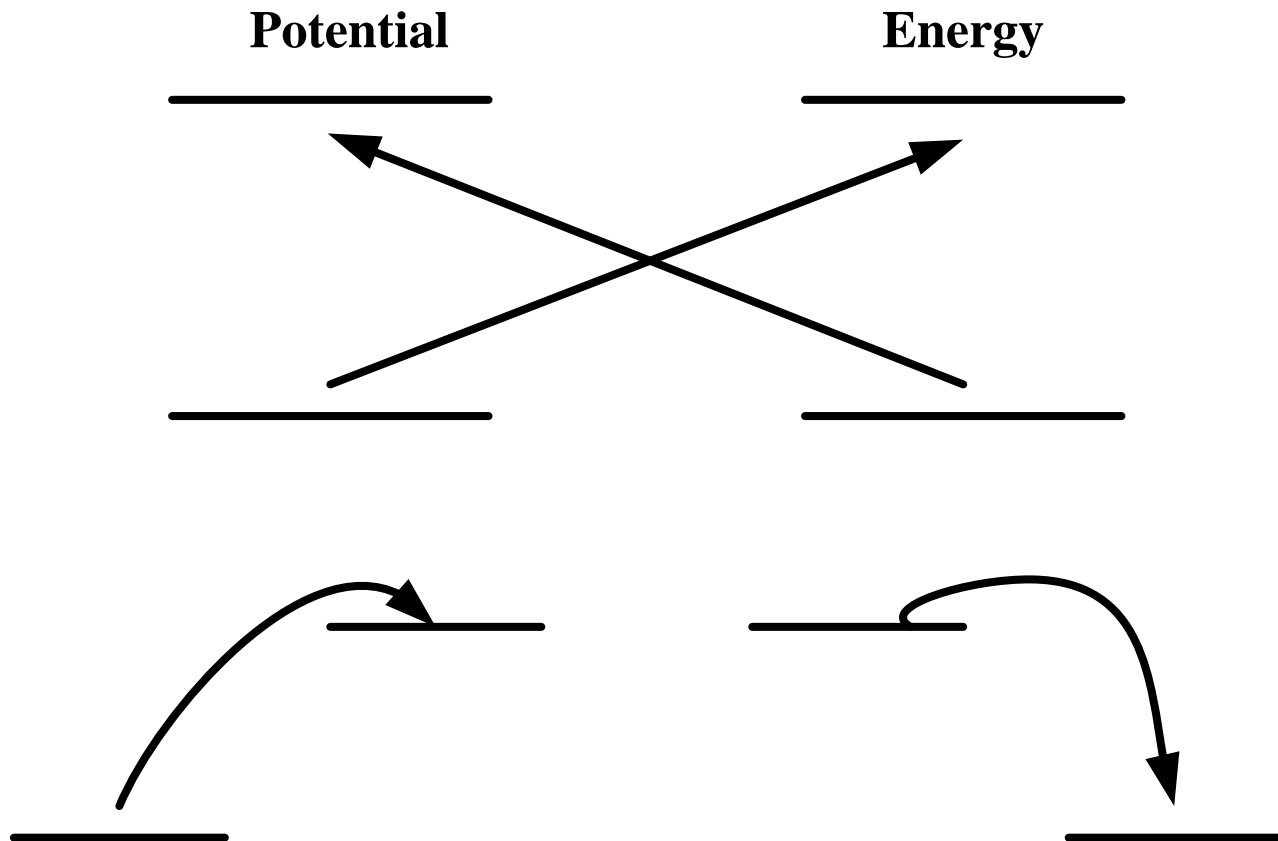
1. Chemical Gibbs free energy (ΔG)
2. Electrochemical Gibbs free energy ($\Delta \hat{G}$)

1) $\Delta \hat{G} = \Delta G + nF\Delta E$



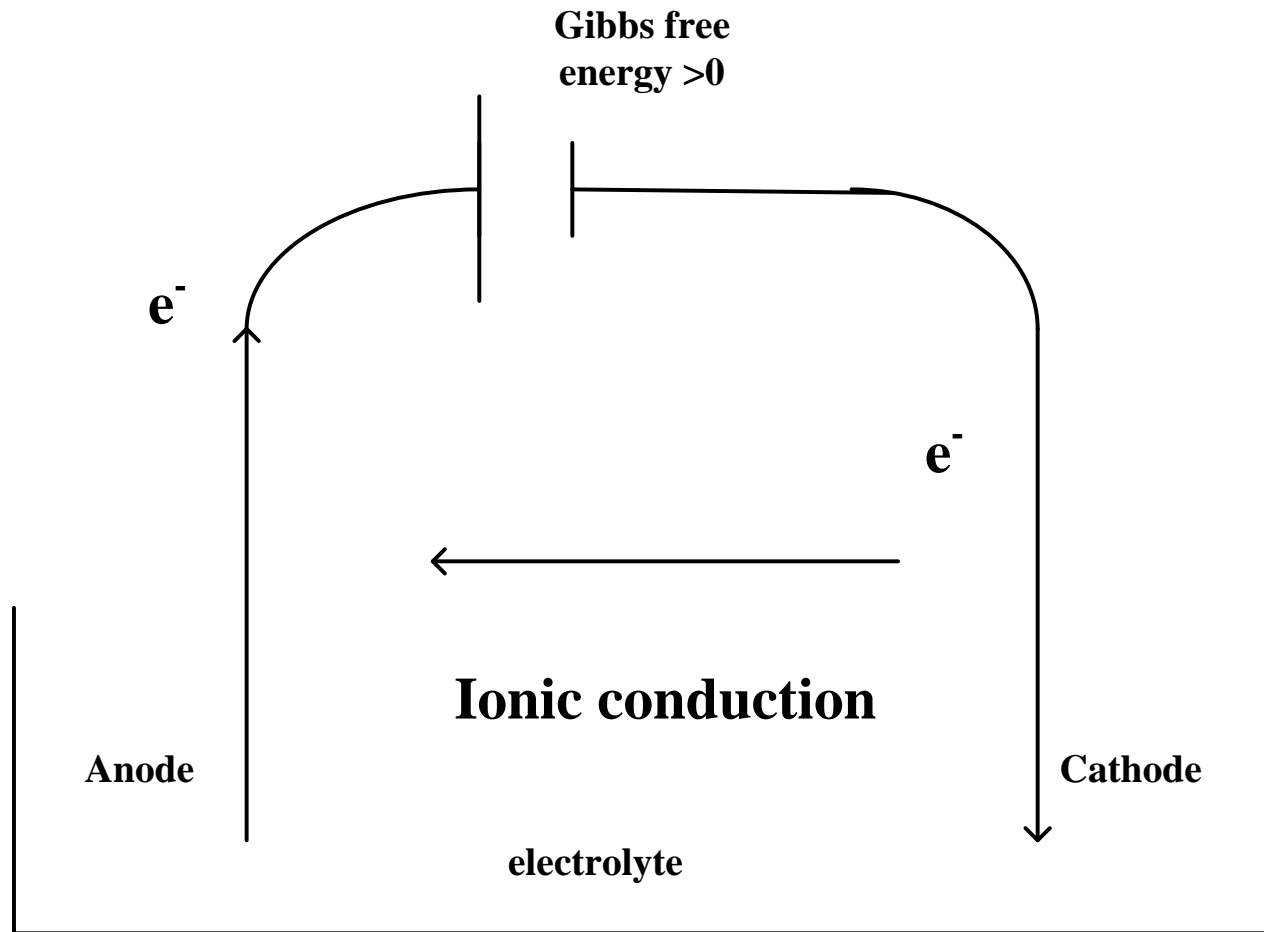
Potential – Energy Relationship

1. High energy ~ Low potential



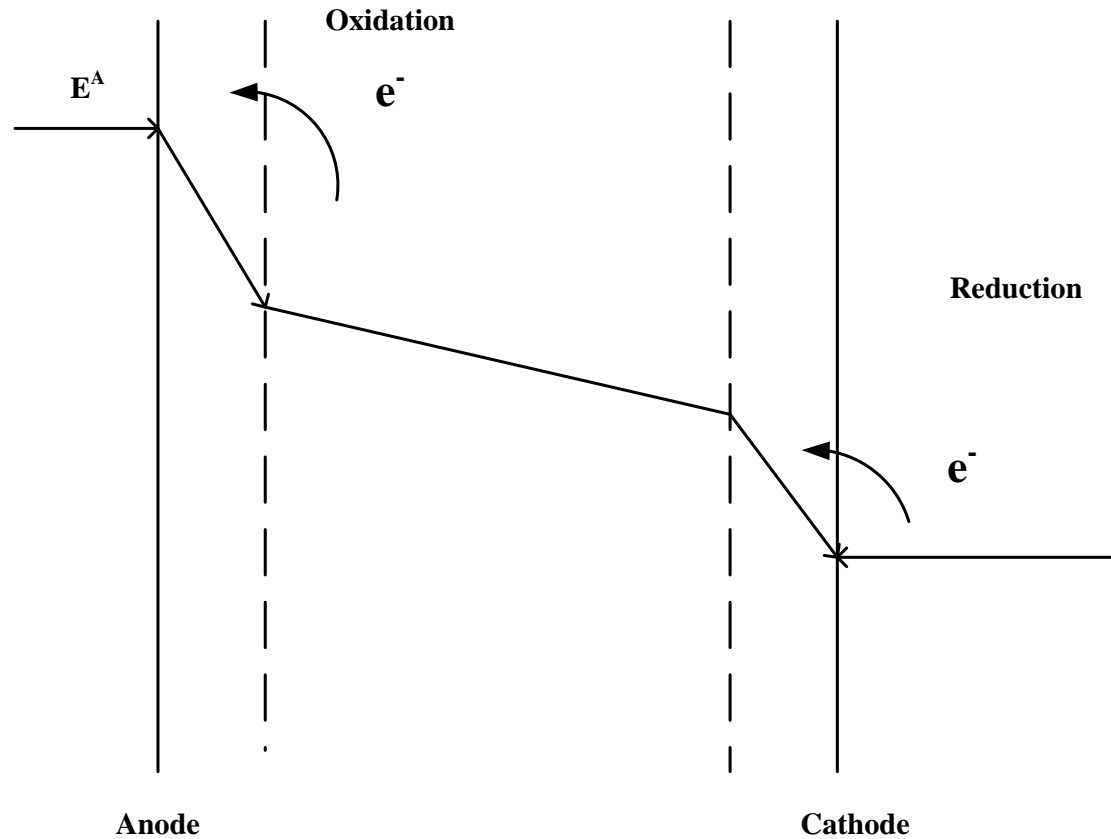
Electrochemical Systems (or Cells)

1. Electrolytic Cell

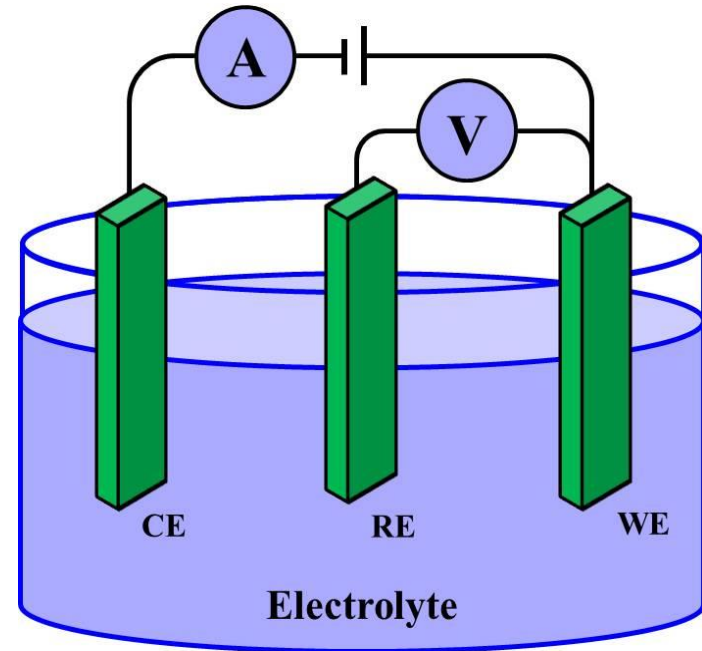
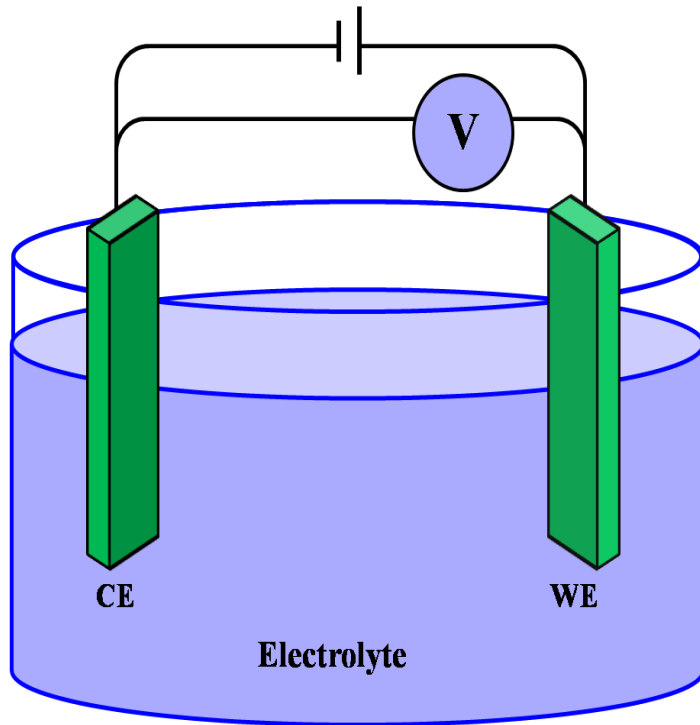


Electrochemical Systems (or Cells)

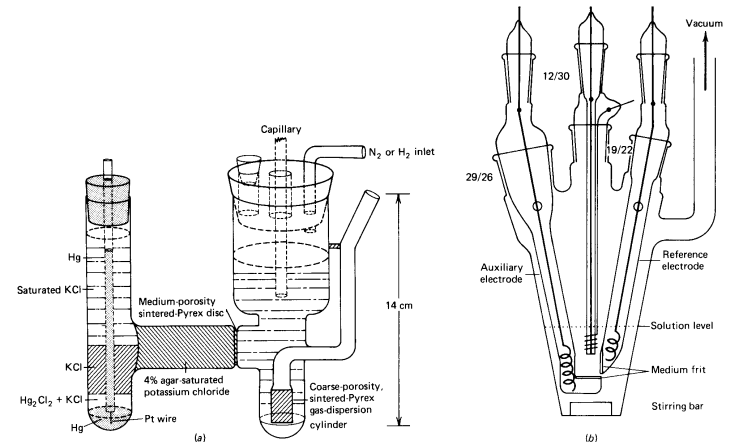
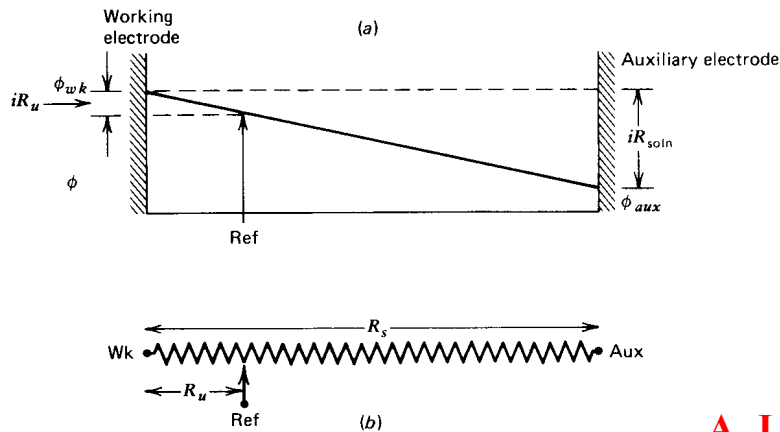
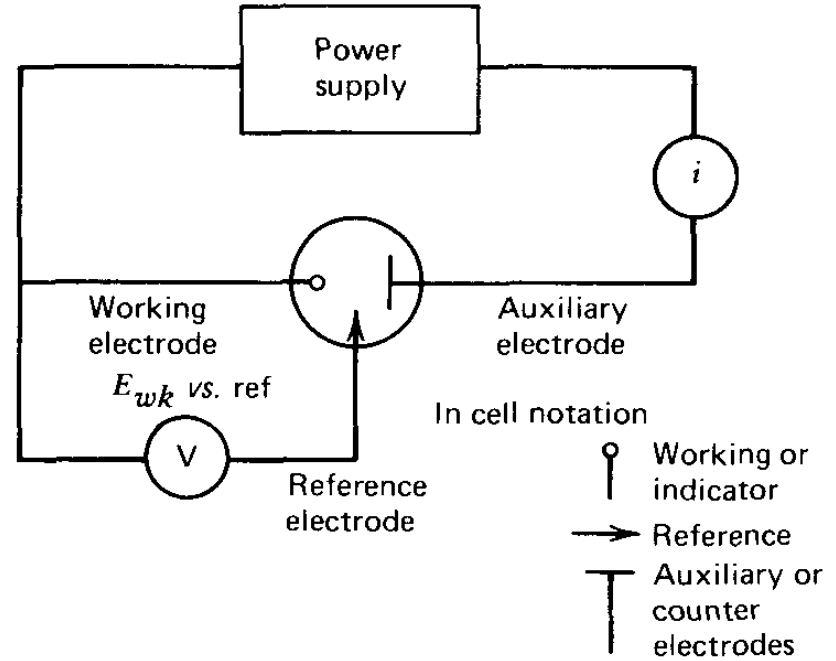
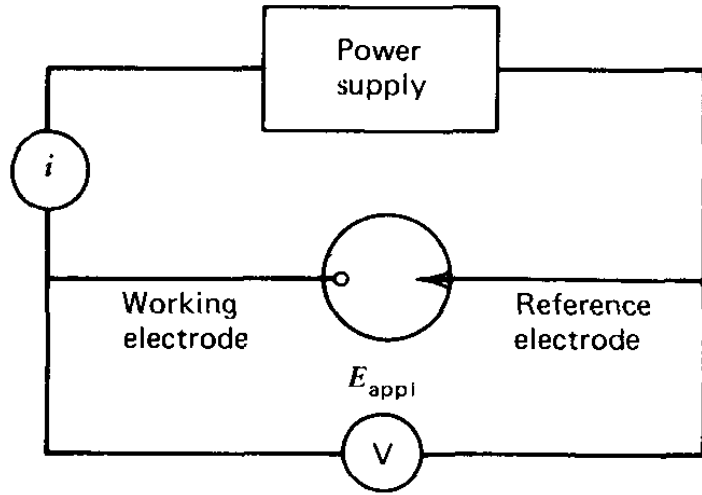
2. Potential drop of a electrolytic cell



Two or three electrode measuring system



Two and three electrode Cells

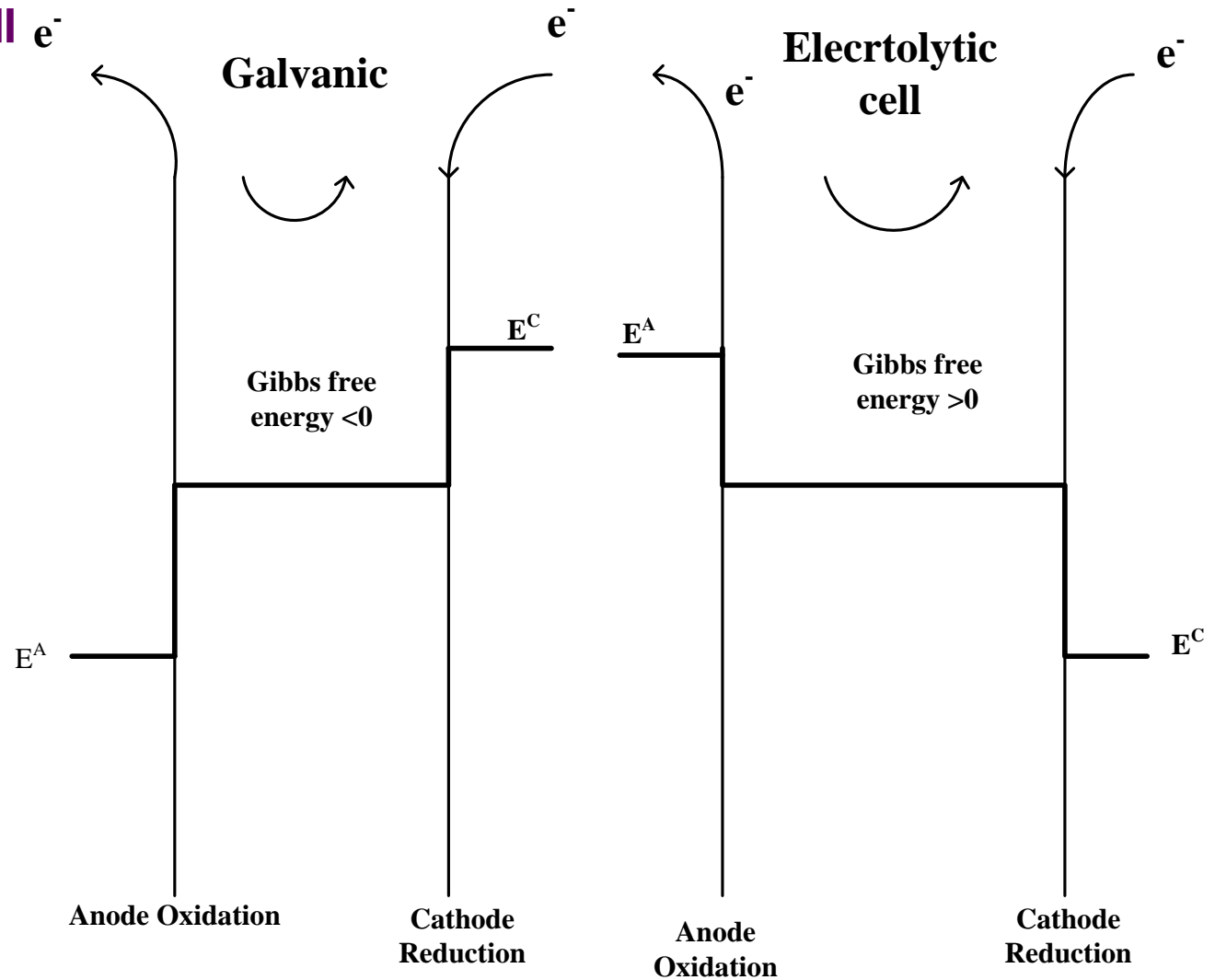


A. J. Bard and L. R. Faulkner, "Electrochemical Methods - Fundamentals and Applications"

Electrochemical Cells

1. Galvanic cell

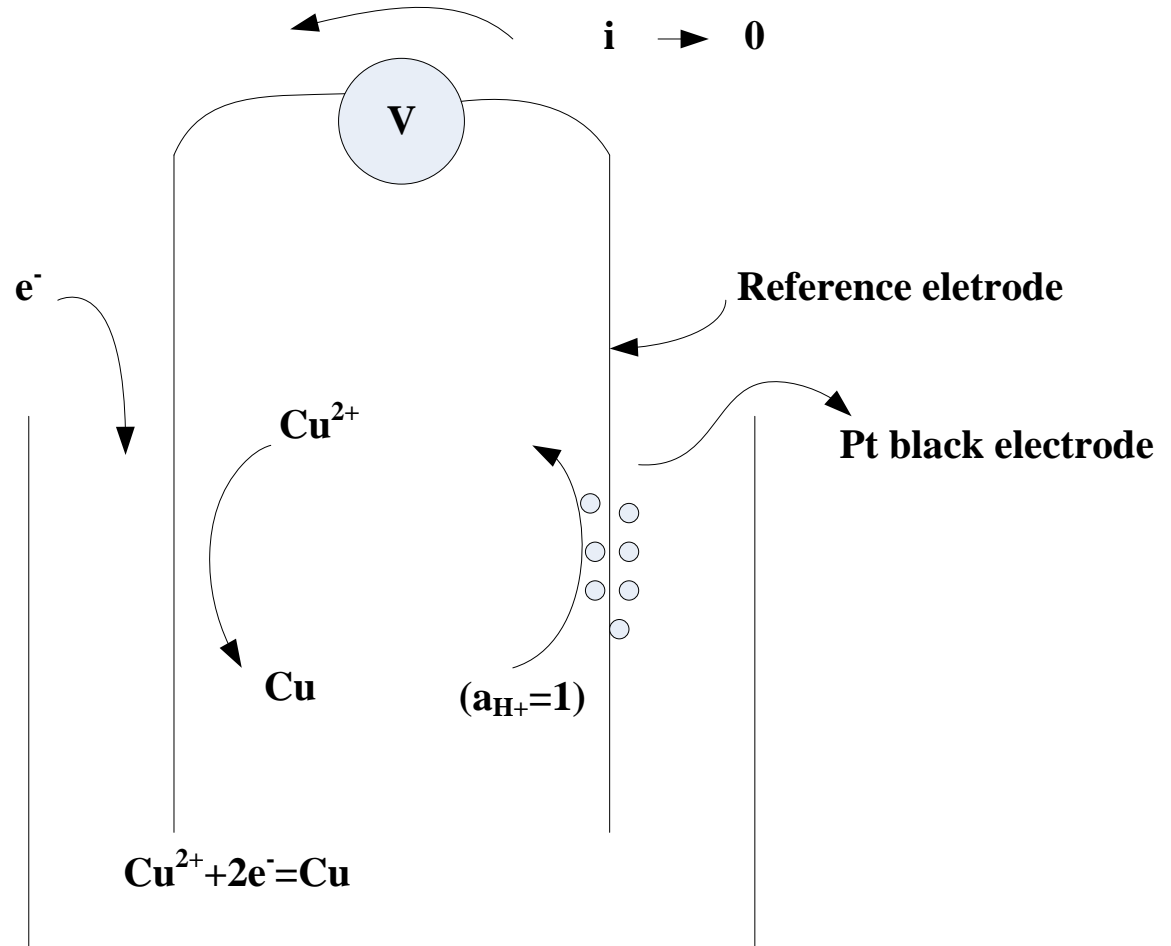
2. Electrolytic cell



Reference Electrodes

1. Stability

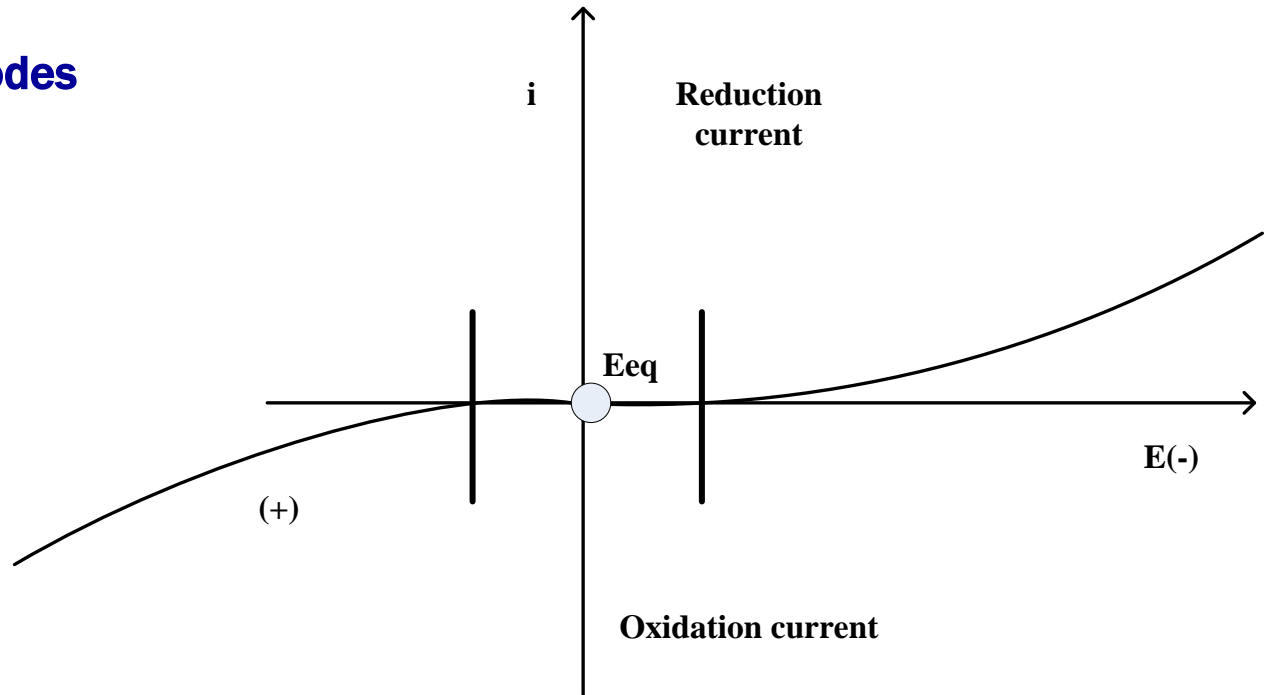
- 1) Temperature coefficients
- 2) Effect of current



Reference Electrodes

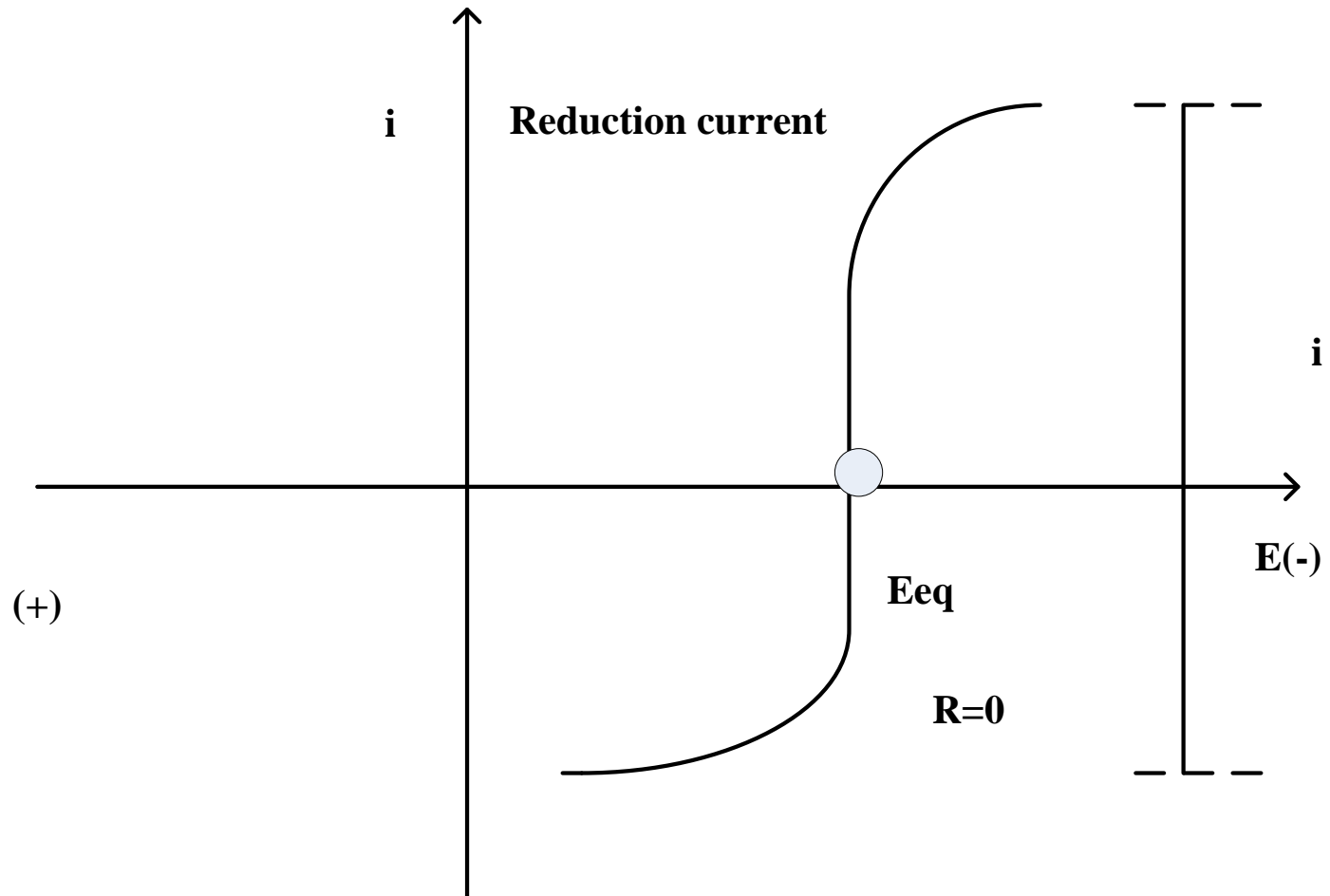
1. i - E curves

- 1) Ideally-polarized electrode
- 2) Ideally-nonpolarized electrode
- 3) General electrodes



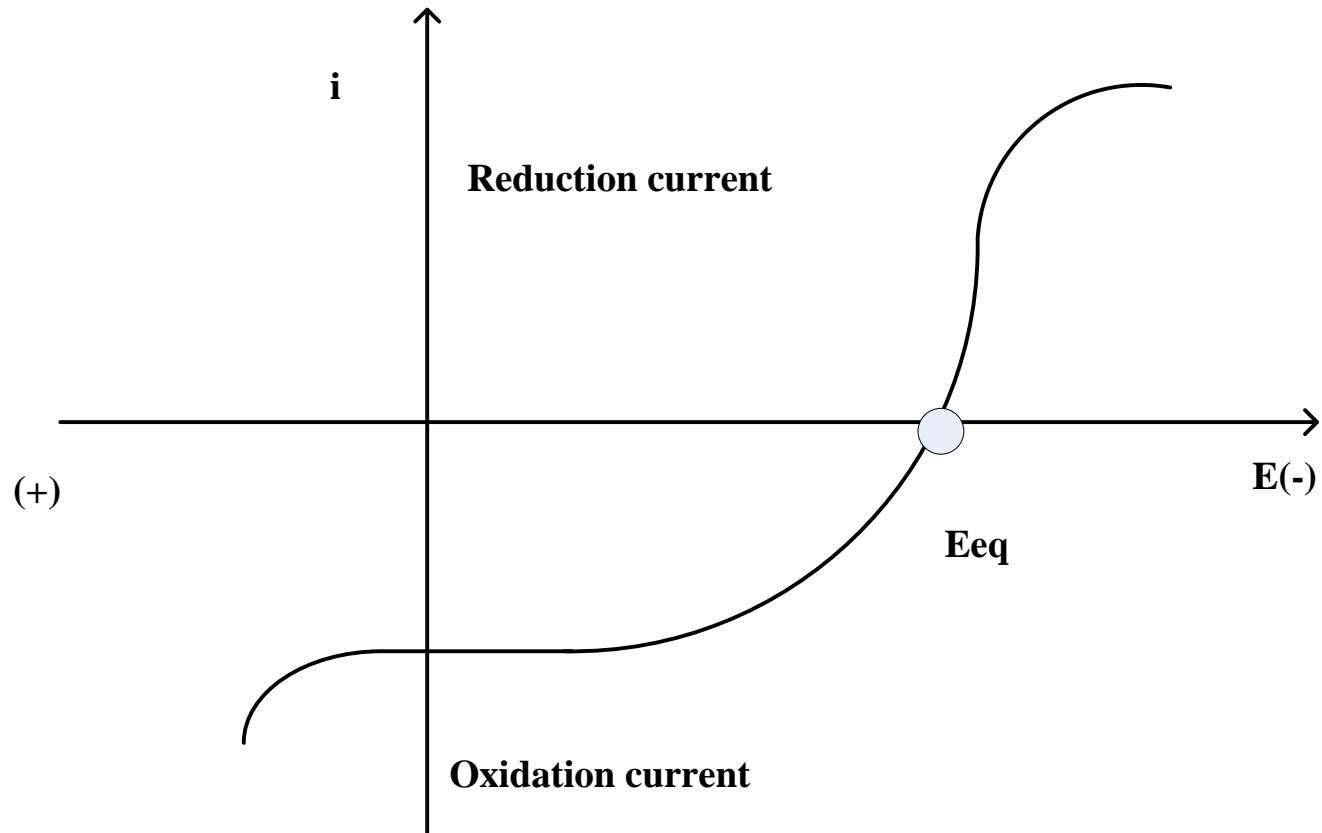
Reference Electrodes

Ideally-non-polarized electrode



Reference electrodes

General i-E curves



Reference electrodes

1. Standard Hydrogen Electrode (SHE)

1) $E = 0. \text{ V}$

2. Saturated Calomel Electrode (SCE)

1) $E = 0.242 \text{ V}$

3. Saturated Ag/AgCl

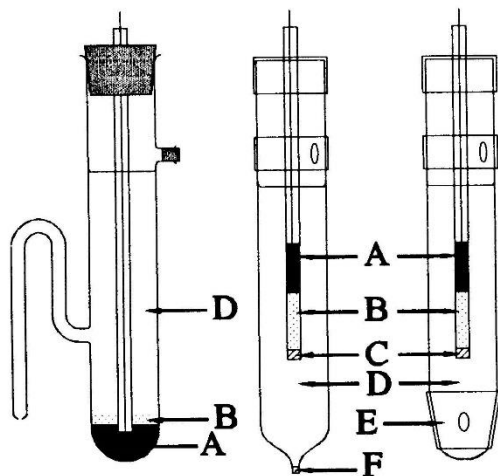
1) $E = 0.197 \text{ V}$

4. Hg/HgO (NaOH, 1M)

1) $E = 0.926 \text{ V}$

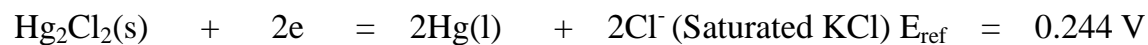
5. Hydroquinone/Quinone

Saturated Calomel electrode (SCE)

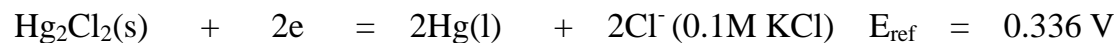


- A = mercury
- B = mercury-calomel paste
- C = asbestos or glass wool plug
- D = potassium chloride solution
- E = sleeve junction
- F = ceramic, quartz or asbestos fiber junction

$$E = E^{\circ} + \frac{RT}{zF} \ln \frac{1}{a_{\text{Cl}^-}}$$



$$\text{Temperature coefficient: } dE_{\text{ref}}/dT = 0.67 \text{ mV K}^{-1}$$



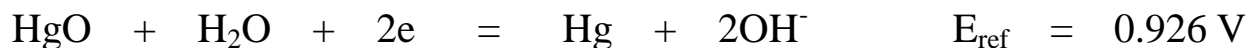
*Temp. coeff
is smaller*

Other Alternative Reference Electrodes

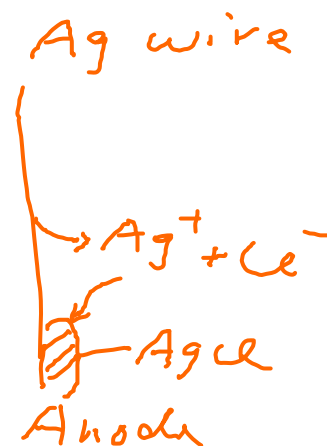
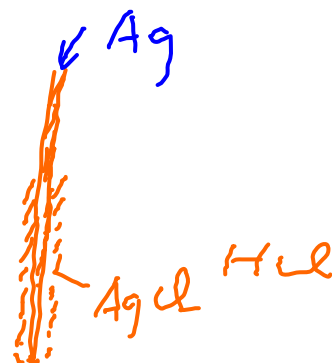
Saturated KCl



$$E = E^{\circ} + \frac{RT}{F} \ln \frac{1}{a_{\text{Cl}^-}}$$



$$E = E^{\circ} + \frac{RT}{F} \ln \frac{1}{a_{\text{OH}^-}}$$

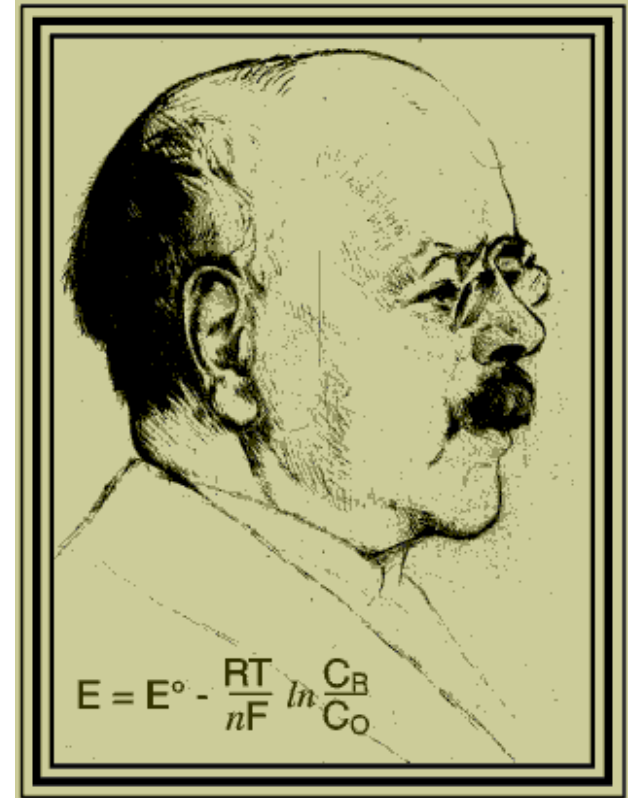
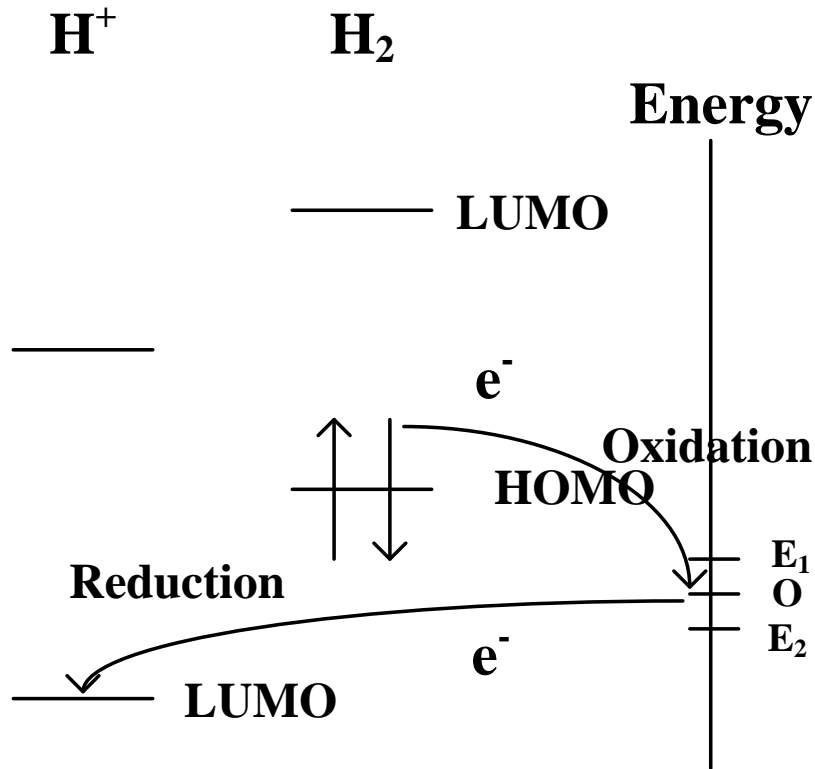


Thermodynamic Equations

1. Nernst equation



$$1) E_{eq} = E_0 + (RT/nF) \ln(C_{O,eq}/C_{R,eq})$$



Electrochemical potential

1. Chemical potential

$$1) \mu_i^\alpha = \mu_i^0 + RT \ln a_i$$

2. Electrochemical potential

$$1) \hat{\mu}_i^\alpha = \hat{\mu}_i^0 + RT \ln a_i + Z_i F \phi_i$$

Electrochemical Potentials

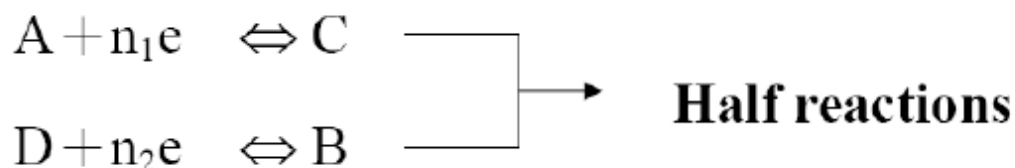




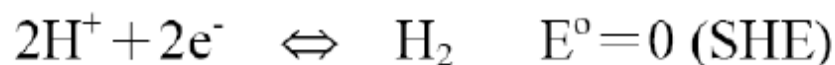
Half reaction and electrode potential



$$\begin{aligned}\Delta E^e = E^e_{\text{cell}} &= E^e_C - E^e_A = \Delta E^o - \frac{RT}{nF} \ln \frac{a^c_C * a^d_D}{a^a_A * a^b_B} \\ &= \left(E^o_C - \frac{RT}{nF} \ln \frac{a^c_C}{a^a_A} \right) - \left(E^o_A - \frac{RT}{nF} \ln \frac{a^b_B}{a^d_D} \right)\end{aligned}$$



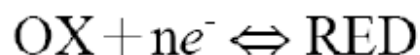
If one half reaction is:



$$\Rightarrow \Delta E^e = E^e_{\text{cell}} = E^e_{\text{half}} = E^o - \frac{RT}{nF} \ln \frac{a^c_C}{a^a_A}$$

$$E_{\text{half}}^e = E^e = E^o + \frac{RT}{nF} \ln \frac{a^a_A}{a^c_C} \quad (\text{electrode potential})$$

For any half reaction



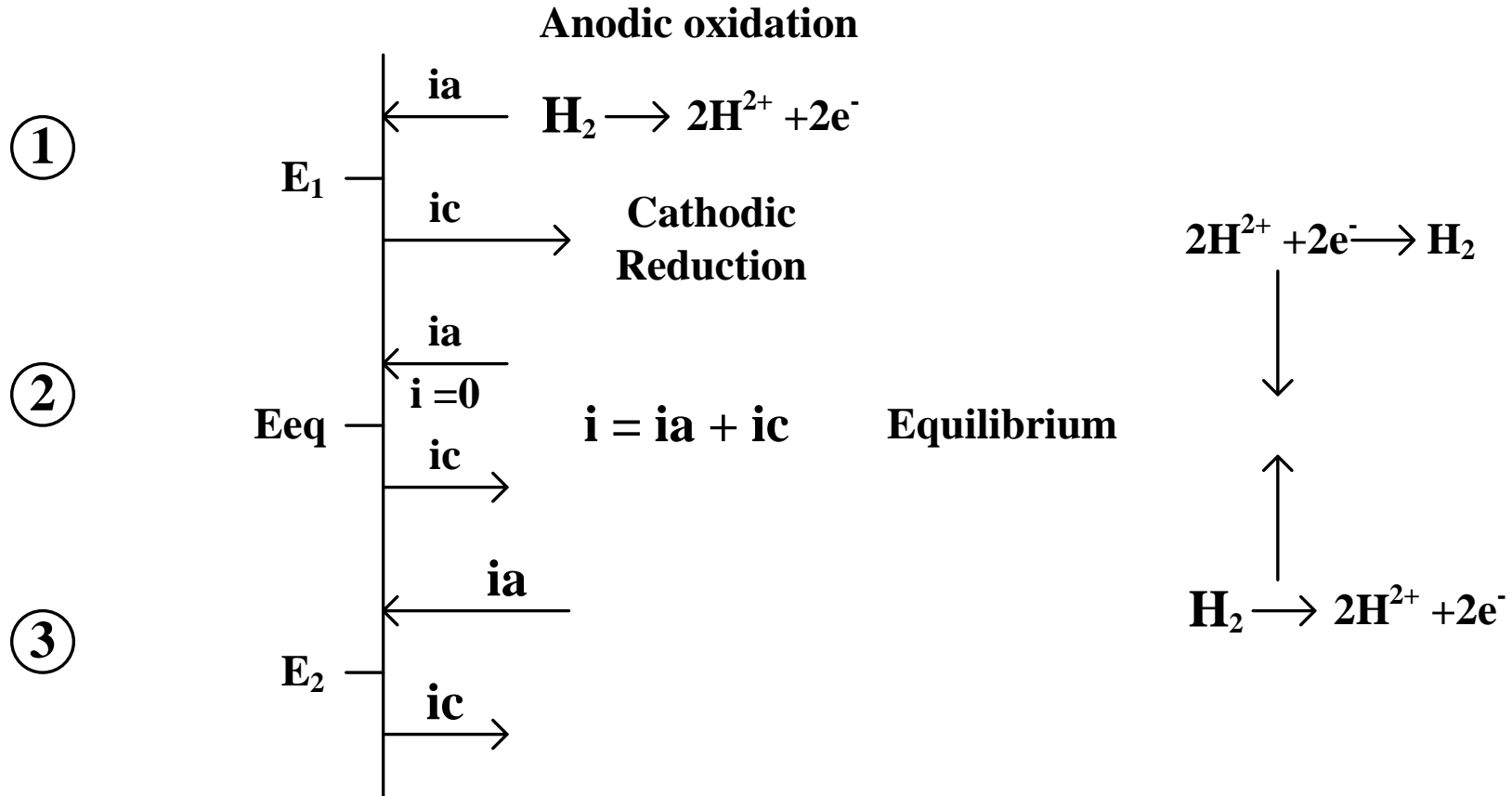
$$\begin{aligned} E^e &= E^o + \frac{RT}{nF} \ln \frac{a_{\text{OX}}}{a_{\text{RED}}} \\ &= E^e = E^o + \frac{RT}{nF} \ln \frac{\gamma_{\text{OX}}}{\gamma_{\text{RED}}} + \frac{RT}{nF} \ln \frac{[\text{OX}]}{[\text{RED}]} \end{aligned}$$

$\gamma_i =$ activity coefficient of i

$$\text{Def: } E^{o'} = E^o + \frac{RT}{nF} \ln \frac{\gamma_{\text{OX}}}{\gamma_{\text{RED}}} \quad (\text{formal potential})$$

Remark: $E^{o'}$ is a function of electrolyte composition.

Equilibrium potential



Standard electrode potentials

Standard electrode potentials (at 25.00°C)

| # | Electrode reaction | E°/V |
|----|--|-------------|
| 1 | $\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) \xrightleftharpoons{\pm 5e^-} \text{Mn}^{2+} (\text{aq}) + 4\text{H}_2\text{O} (\ell)$ | +1.512 |
| 2 | $\text{Cl}_2 (\text{g}) \xrightleftharpoons{\pm 2e^-} 2\text{Cl}^- (\text{aq})$ | +1.3578 |
| 3 | $\text{Cr}_2\text{O}_7^{2-} (\text{aq}) + 14\text{H}^+ (\text{aq}) \xrightleftharpoons{\pm 6e^-} 2\text{Cr}^{3+} (\text{aq}) + 7\text{H}_2\text{O} (\ell)$ | +1.33 |
| 4 | $\text{O}_2 (\text{g}) + 4\text{H}^+ (\text{aq}) \xrightleftharpoons{\pm 4e^-} 2\text{H}_2\text{O} (\ell)$ | +1.2288 |
| 5 | $\text{Ag}^+ (\text{aq}) \xrightleftharpoons{\pm e^-} \text{Ag} (\text{s})$ | +0.7989 |
| 6 | $\text{Hg}_2^{2+} (\text{aq}) \xrightleftharpoons{\pm 2e^-} 2\text{Hg} (\ell)$ | +0.7958 |
| 7 | $\text{Fe}^{3+} (\text{aq}) \xrightleftharpoons{\pm e^-} \text{Fe}^{2+} (\text{aq})$ | +0.771 |
| 8 | $\text{O}_2 (\text{g}) + 2\text{H}^+ (\text{aq}) \xrightleftharpoons{\pm 2e^-} \text{H}_2\text{O}_2 (\text{aq})$ | +0.6946 |
| 9 | $\text{I}_3^- (\text{aq}) \xrightleftharpoons{\pm 2e^-} 3\text{I}^- (\text{aq})$ | +0.5362 |
| 10 | $\text{O}_2 (\text{g}) + 2\text{H}_2\text{O} (\ell) \xrightleftharpoons{\pm 4e^-} 4\text{OH}^- (\text{aq})$ | +0.4008 |
| 11 | $\text{Fe}(\text{CN})_6^{3-} (\text{aq}) \xrightleftharpoons{\pm e^-} \text{Fe}(\text{CN})_6^{4-} (\text{aq})$ | +0.355 |
| 12 | $\text{Ag}_2\text{O} (\text{s}) + \text{H}_2\text{O} (\ell) \xrightleftharpoons{\pm 2e^-} 2\text{Ag} (\text{s}) + 2\text{OH}^- (\text{aq})$ | +0.3428 |
| 13 | $\text{Cu}^{2+} (\text{aq}) \xrightleftharpoons{\pm 2e^-} \text{Cu} (\text{s})$ | +0.340 |
| 14 | $\text{Hg}_2\text{Cl}_2 (\text{s}) \xrightleftharpoons{\pm 2e^-} 2\text{Hg} (\ell) + 2\text{Cl}^- (\text{aq})$ | +0.2680 |
| 15 | $\text{AgCl} (\text{s}) \xrightleftharpoons{\pm e^-} \text{Ag} (\text{s}) + \text{Cl}^- (\text{aq})$ | +0.22216 |
| 16 | $2\text{H}^+ (\text{aq}) \xrightleftharpoons{\pm 2e^-} \text{H}_2 (\text{g})$ | 0 |
| 17 | $\text{Pb}^{2+} (\text{aq}) \xrightleftharpoons{\pm 2e^-} \text{Pb} (\text{Hg})$ | -0.1207 |
| 18 | $\text{V}^{3+} (\text{aq}) \xrightleftharpoons{\pm e^-} \text{V}^{2+} (\text{aq})$ | -0.255 |
| 19 | $\text{Zn}^{2+} (\text{aq}) \xrightleftharpoons{\pm 2e^-} \text{Zn} (\text{s})$ | -0.7628 |
| 20 | $2\text{H}_2\text{O} (\ell) \xrightleftharpoons{\pm 2e^-} \text{H}_2 (\text{g}) + 2\text{OH}^- (\text{aq})$ | -0.8280 |

$$a_{\text{H}^+} = 1$$

$$T = 25^\circ\text{C}$$

(Reversible)
Equilibrium Electrode potential

$$E = E^\circ + \frac{RT}{F} \ln a_{\text{Ag}^+}$$

↑

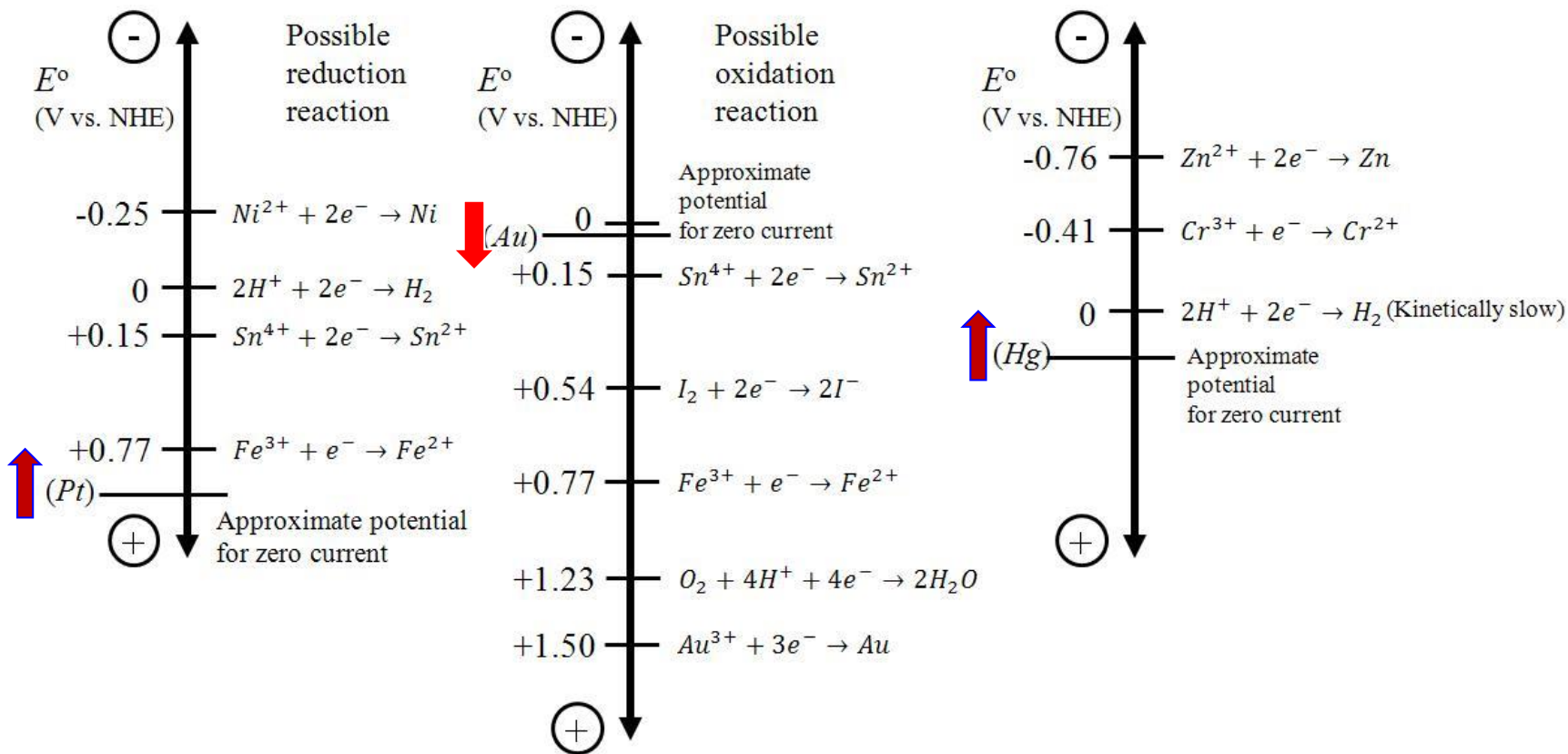
0.7989

if $a_{\text{Ag}^+} > 1$

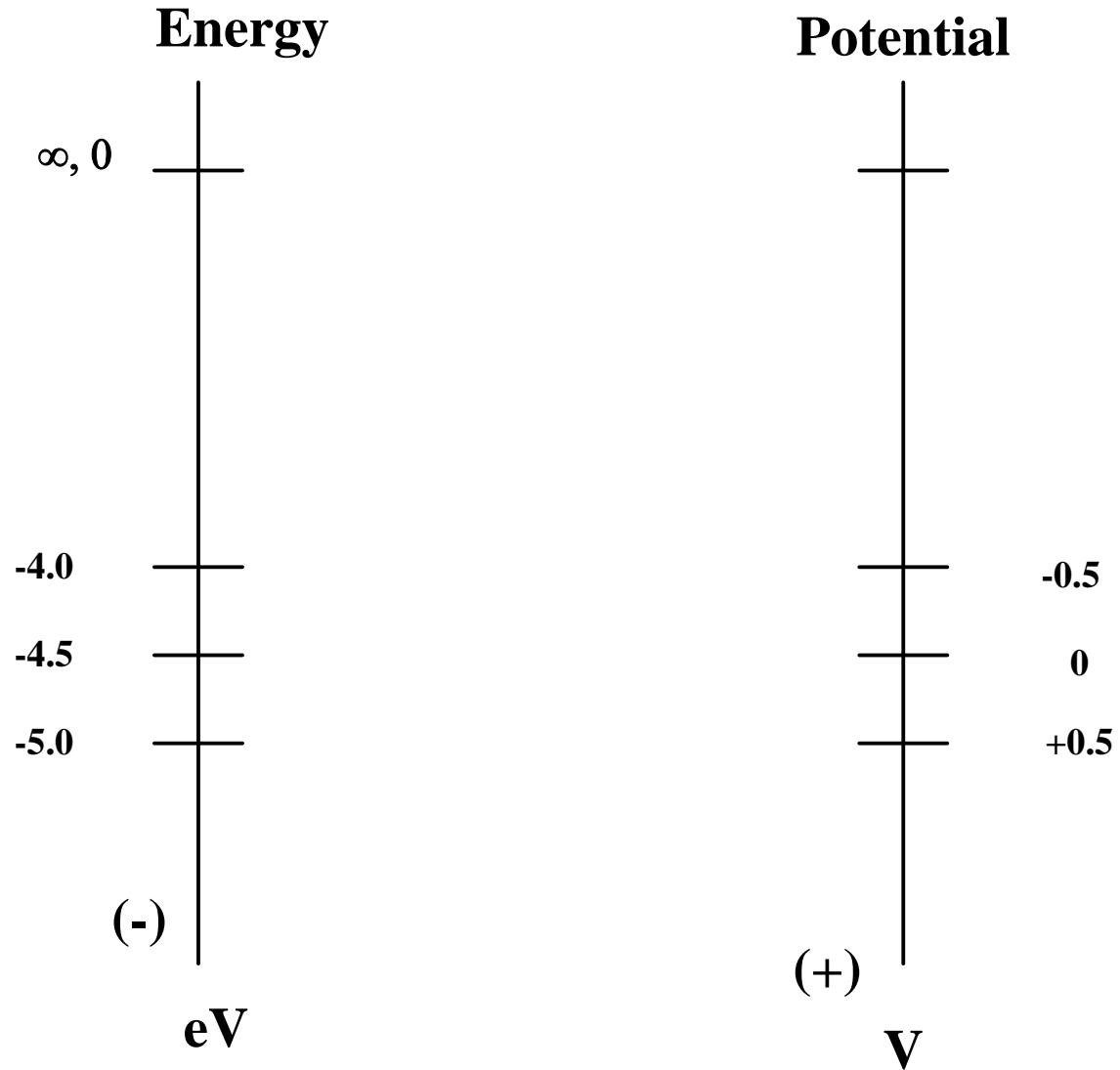
$$\rightarrow E > E^\circ$$

SHE

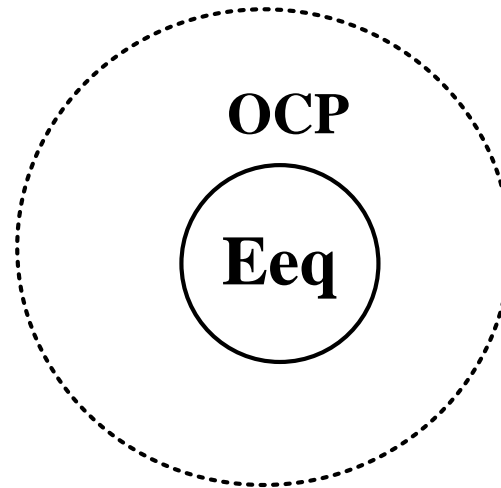
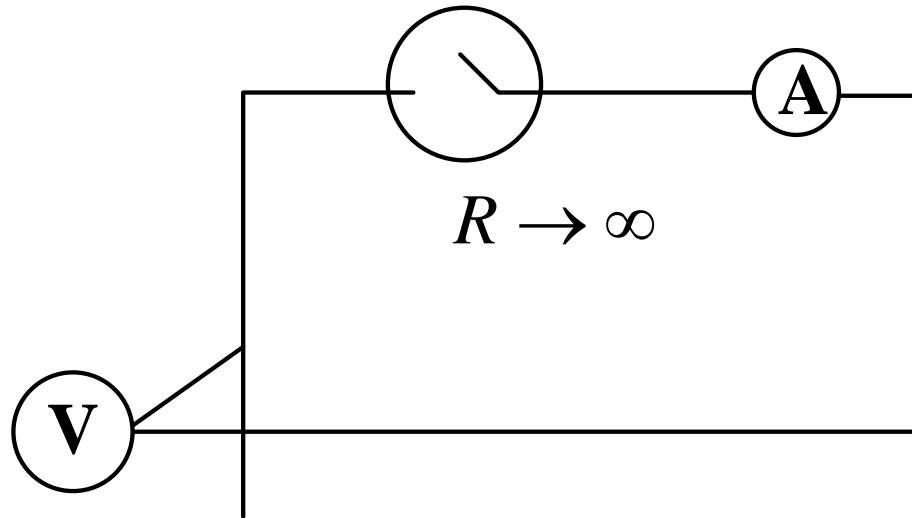
Electrochemical Potentials



Potential vs. Energy

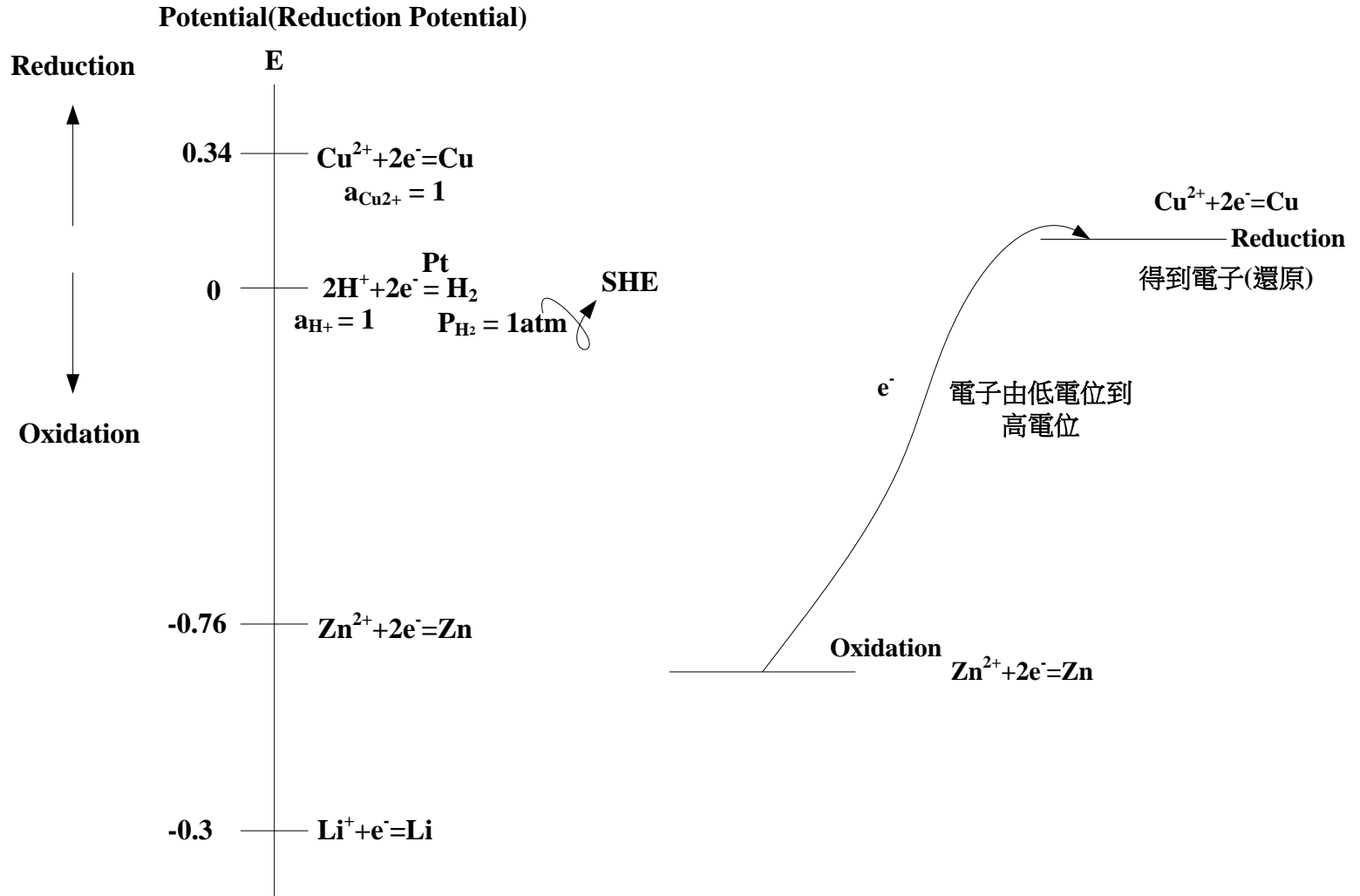


Open Circuit Potential



Reduction Potential

1. Potential



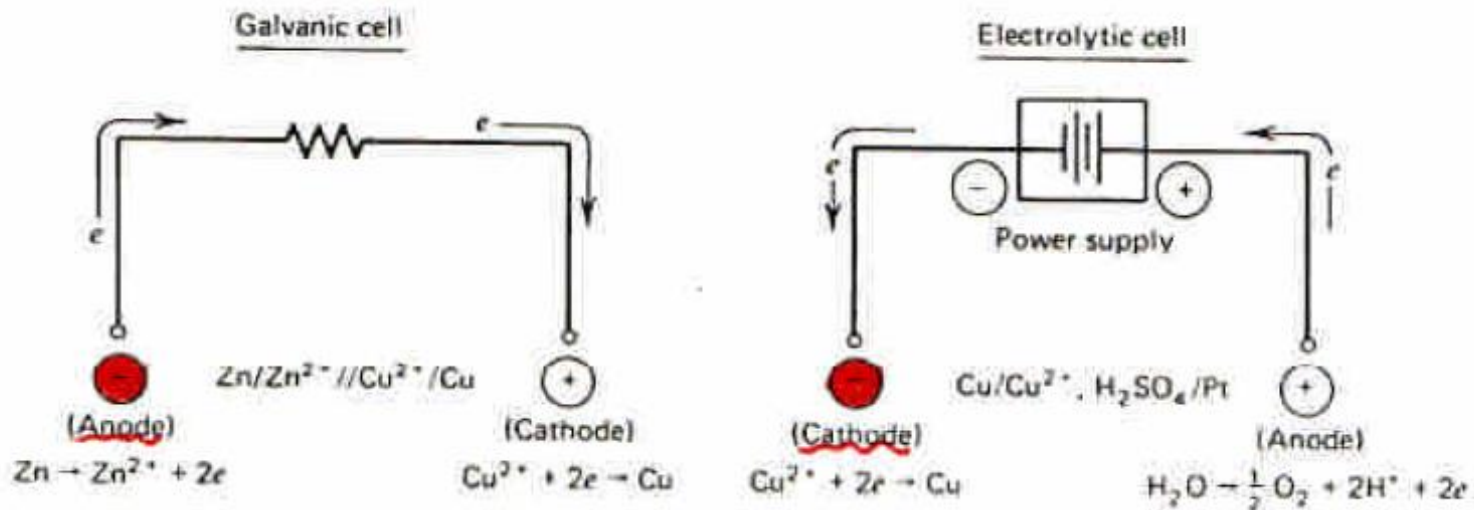
Types of cell ($\Delta G = -nFE_{\text{cell}}$)

1. Galvanic cell ($\Delta G < 0$; $E_{\text{cell}} > 0$)
 - 1) Batteries
 - 2) Fuel cells
 - 3) Corrosion
 - 4) Others
2. Electrolytic cell ($\Delta G > 0$; $E_{\text{cell}} < 0$)
 - 1) Electro-synthesis
 - 2) Electro-deposition
 - 3) Electro-coating
 - 4) Electro-etching
 - 5) Others

$$\Delta G = -nFE_{\text{cell}}$$

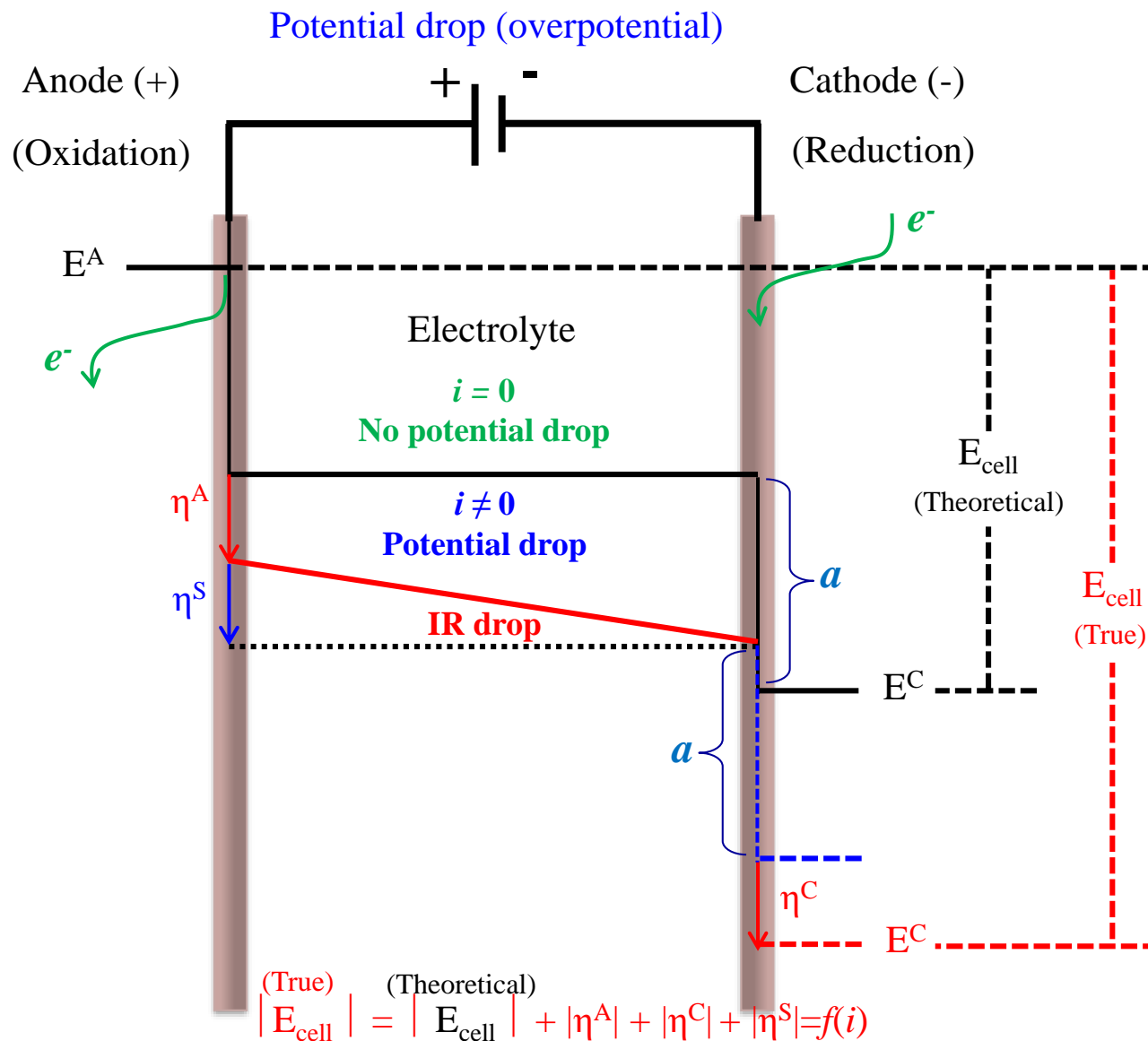
Galvanic Cell: Electrochemical reactions take place spontaneously. $\Delta G = -nEF$; $\Delta G < 0 \Leftrightarrow$ spontaneous
 (1) E : potential difference between cathode and anode
 (2) Valid under equilibrium (no net currents)

Electrolytic Cell: Electrochemical reactions do not take place spontaneously.



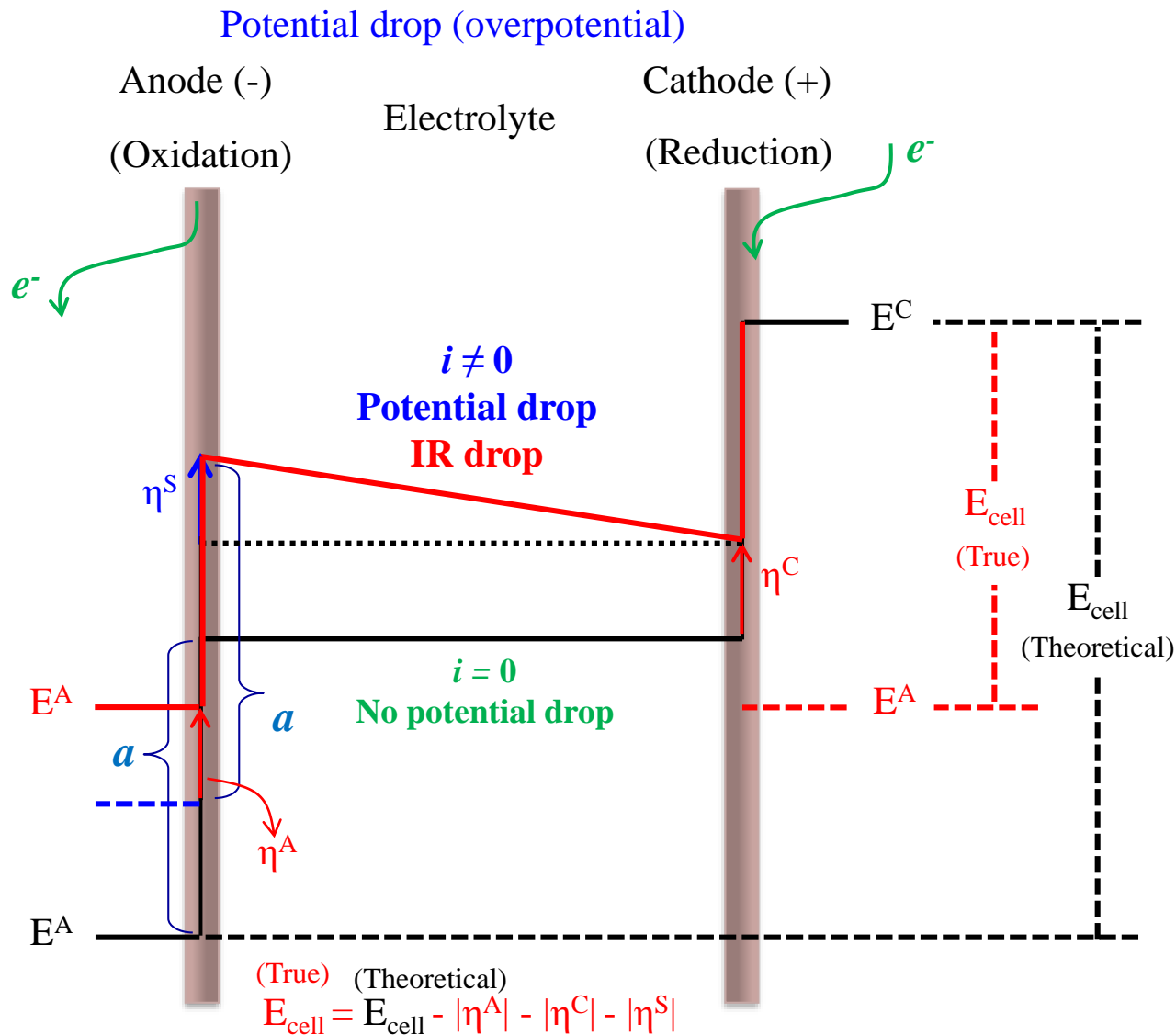
Potential Drop in Electrolytic cell

Electrolytic cell ($\Delta G > 0$)

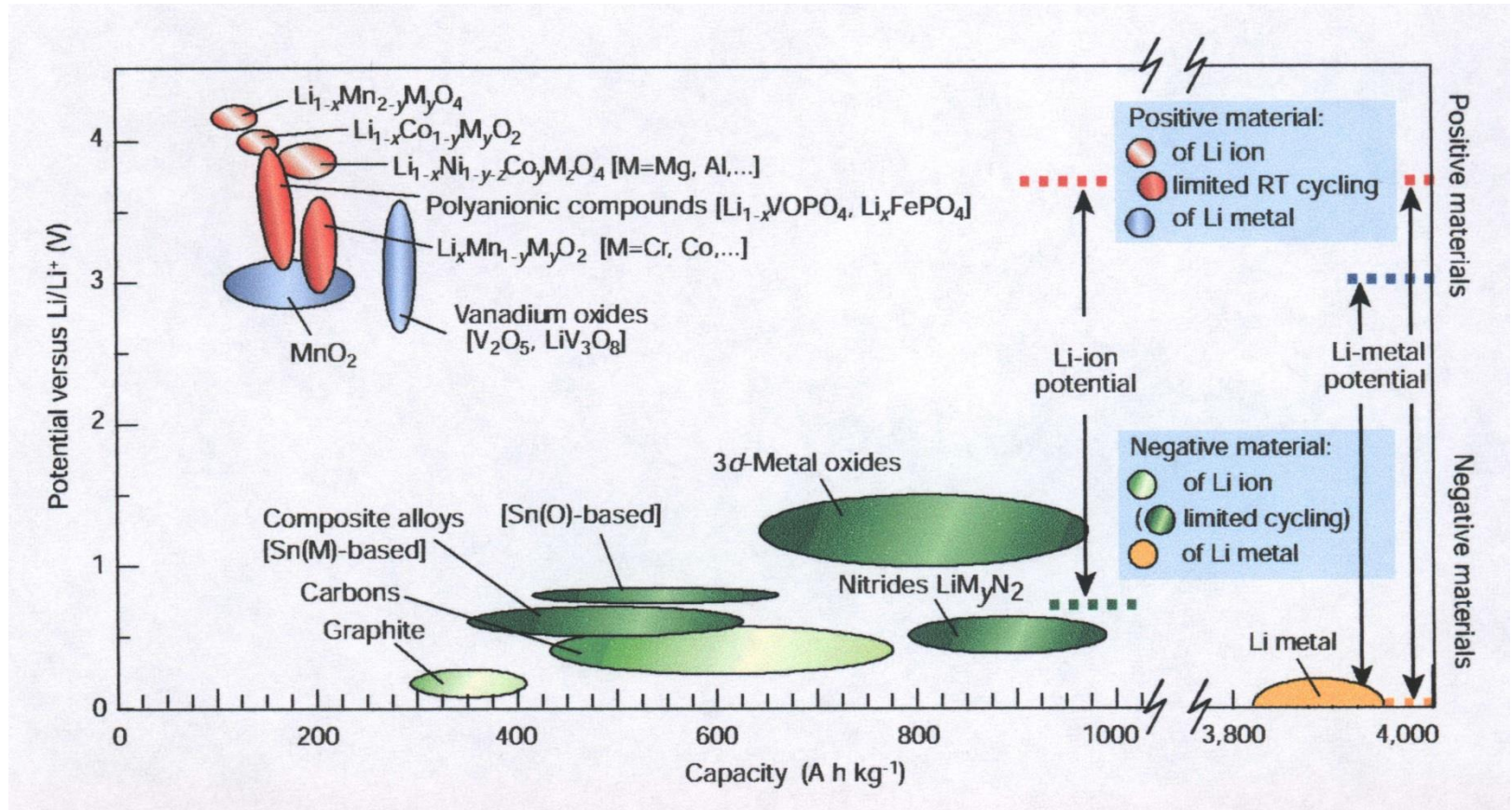


Potential Drop in Galvanic cell

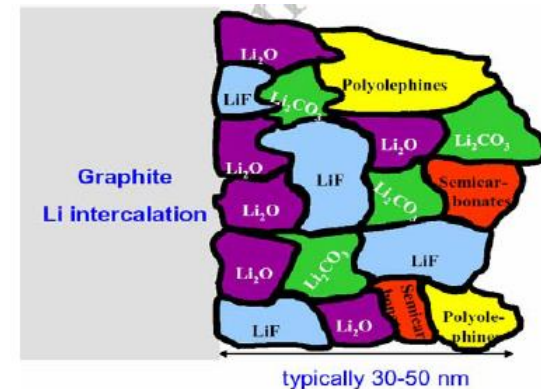
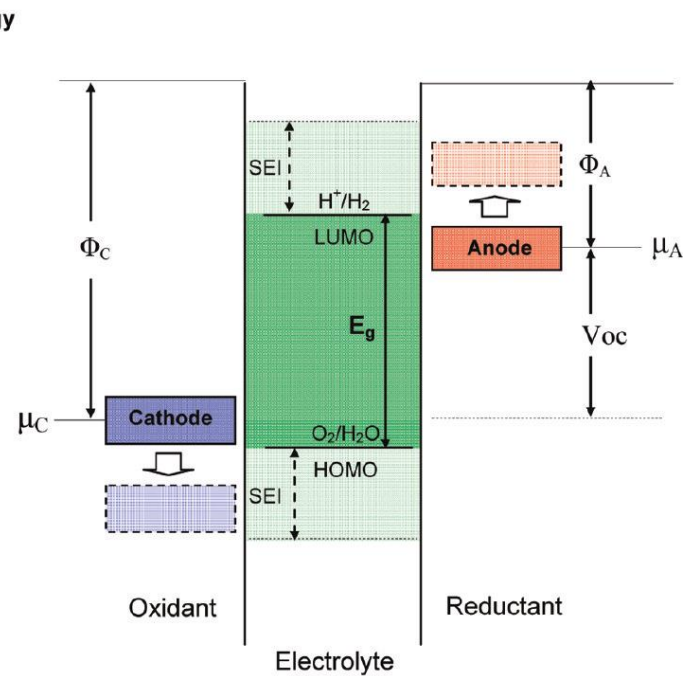
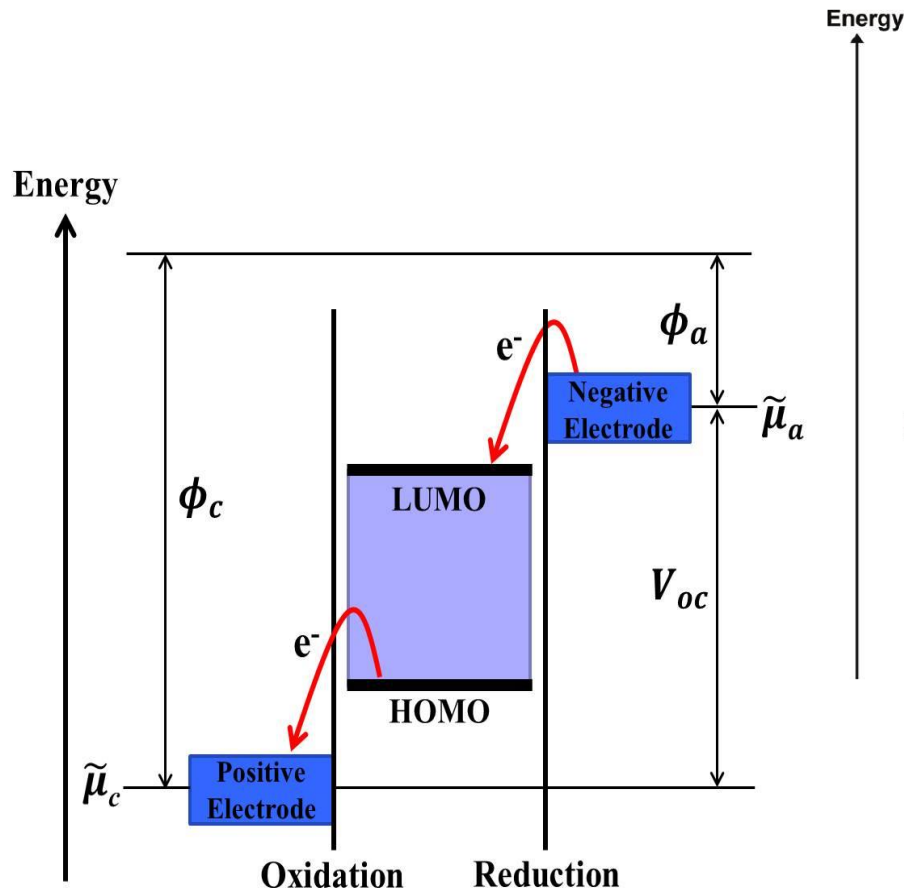
Galvanic cell ($\Delta G < 0$)



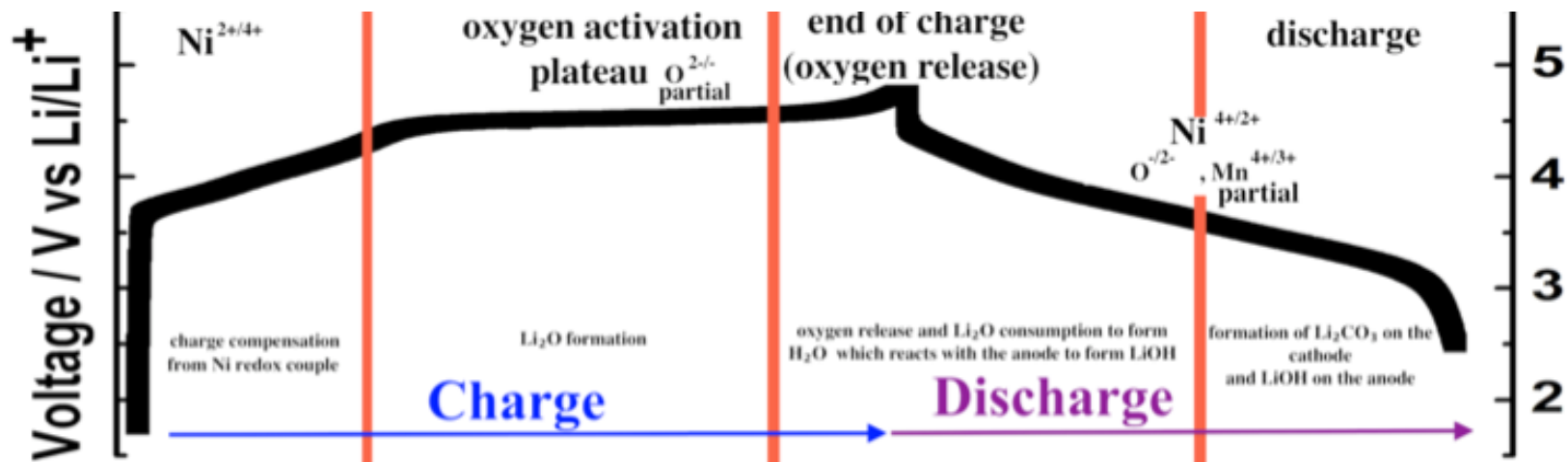
Voltage vs. Capacity for positive and negative-electrode materials



Interfacial Phenomena

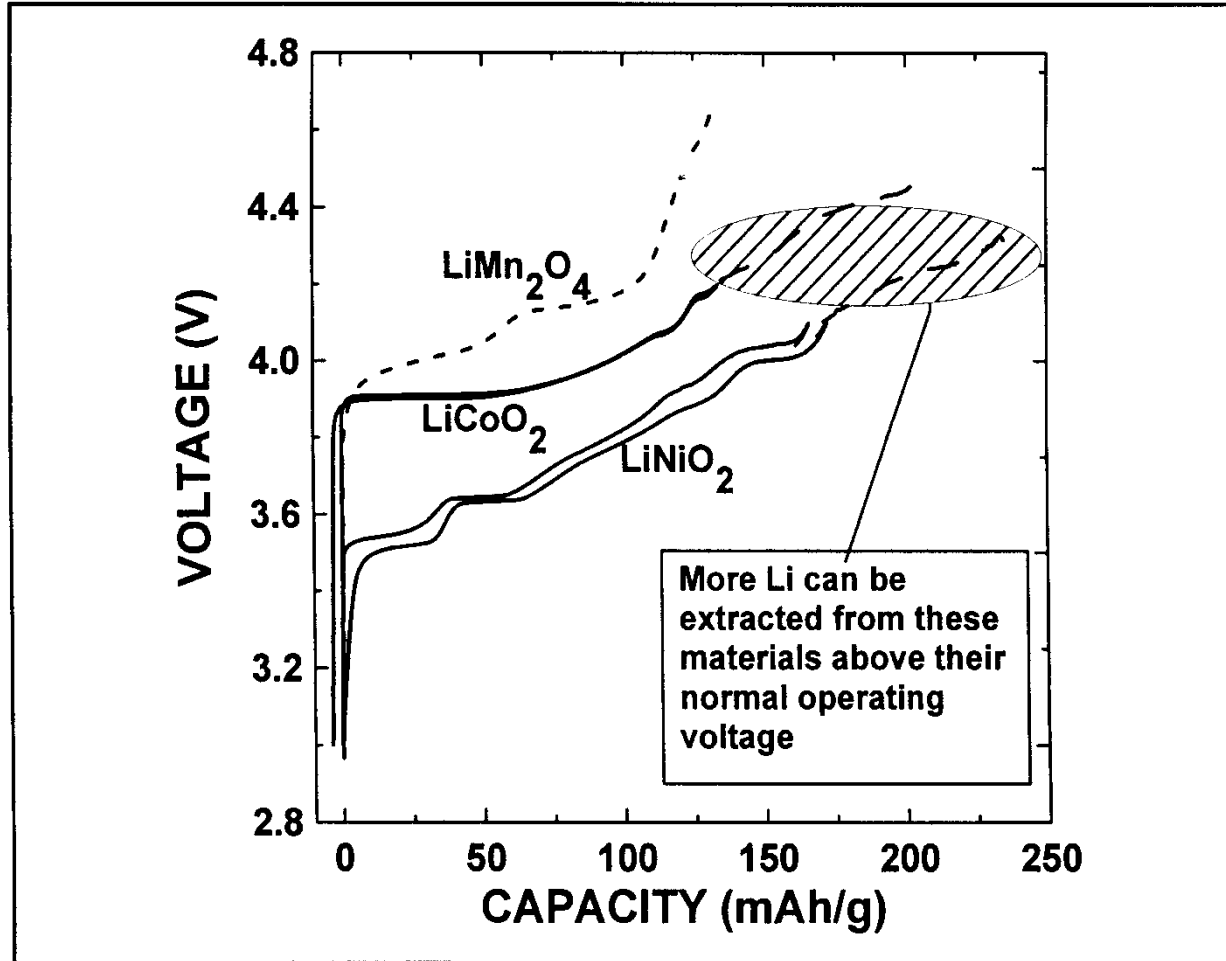


Lithium-rich high-capacity cathode



- **Li-rich compounds**
- **High capacity >250 mAh/g**
- **Unconventional charging mechanism**
- **High 1st Irreversible capacity**
- **Voltage-fading and hysteresis**

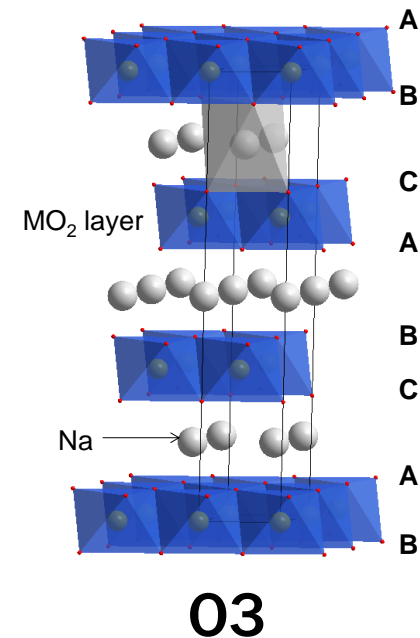
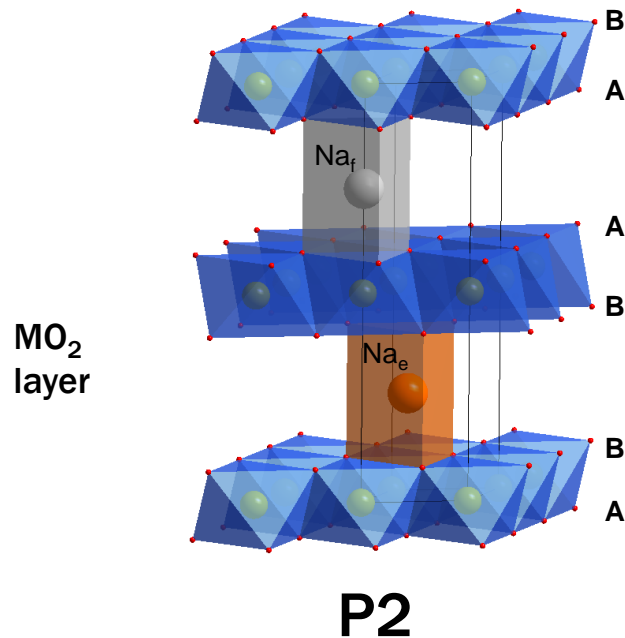
Charging-Behaviors



Layered Sodium Metal Oxides

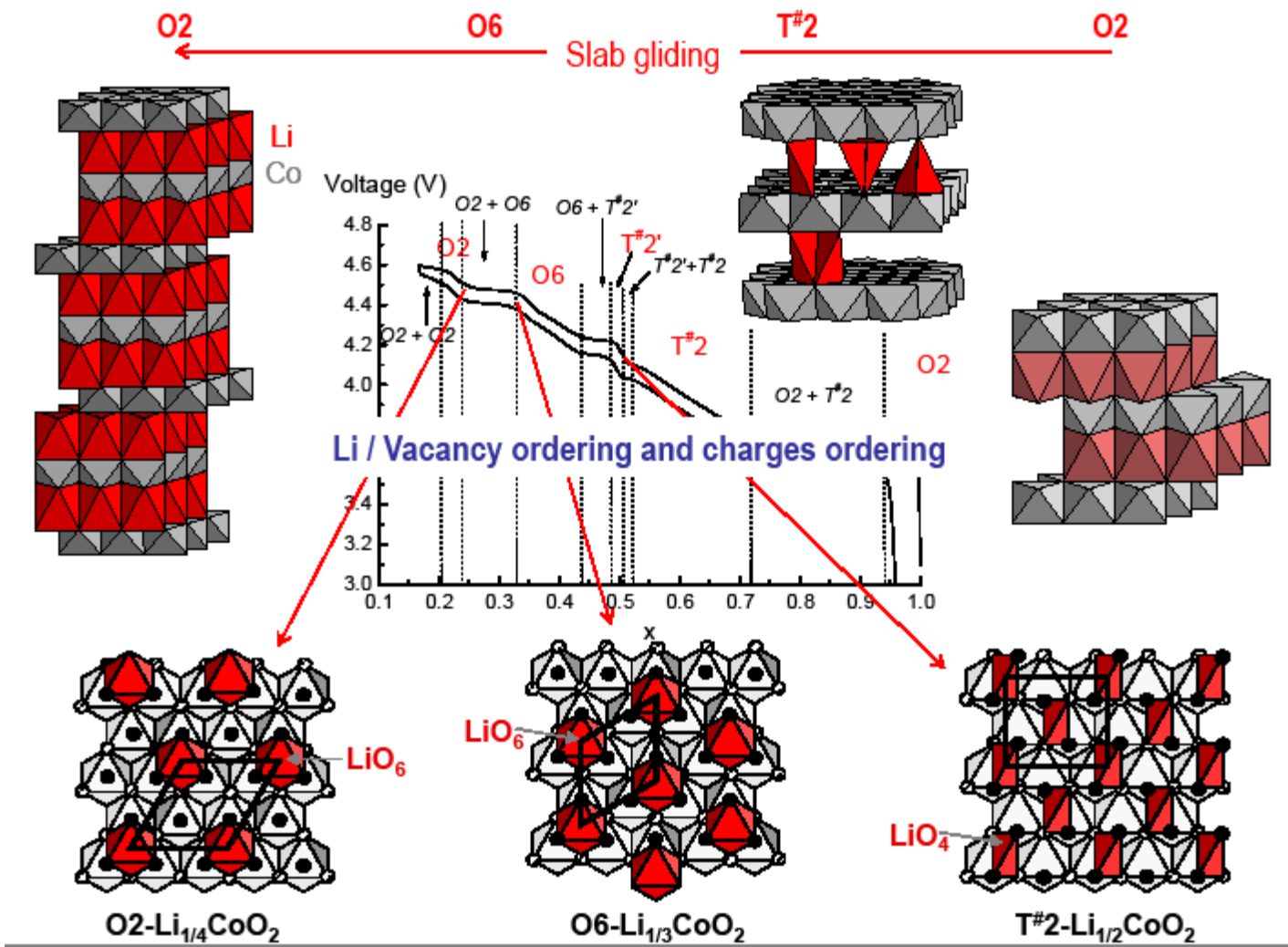
The Nomenclature of Layered Sodium Metal Oxides

- The layered oxides are classified depending on:
 - The site occupied by the alkali ion (**P**rismatic or **O**ctahedral)
 - The number MO_2 slabs / hexagonal cell

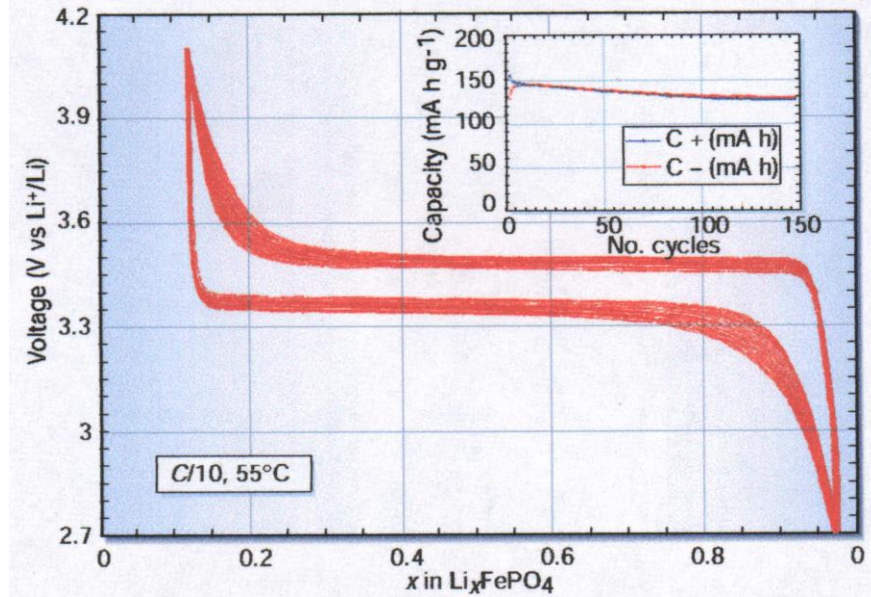
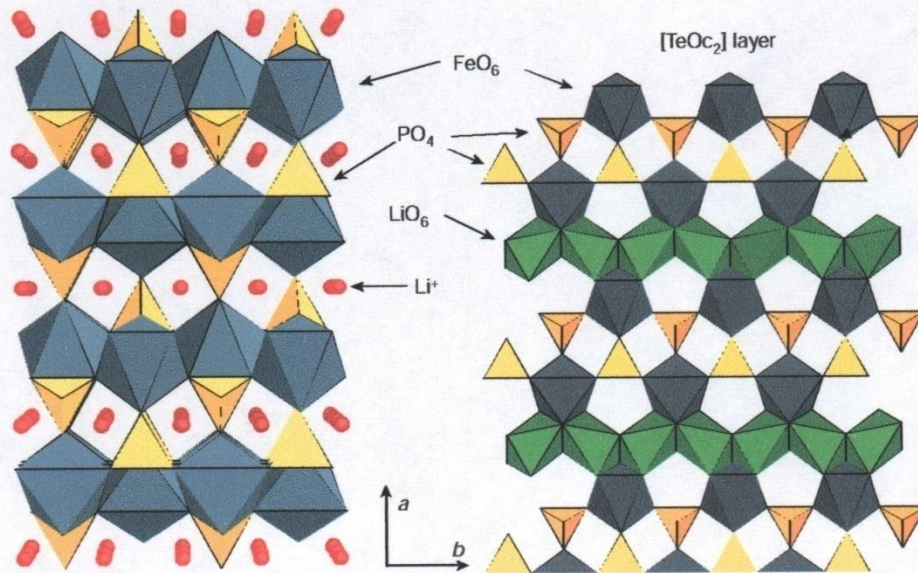


- There is also P3 phases (sodium ion in a prismatic environment, with 3 MO_6 slabs/cell), O'3 phases (the prime sign stands for a distortion occurring in the cell), ...

Potential Curve vs. Structural Evolution

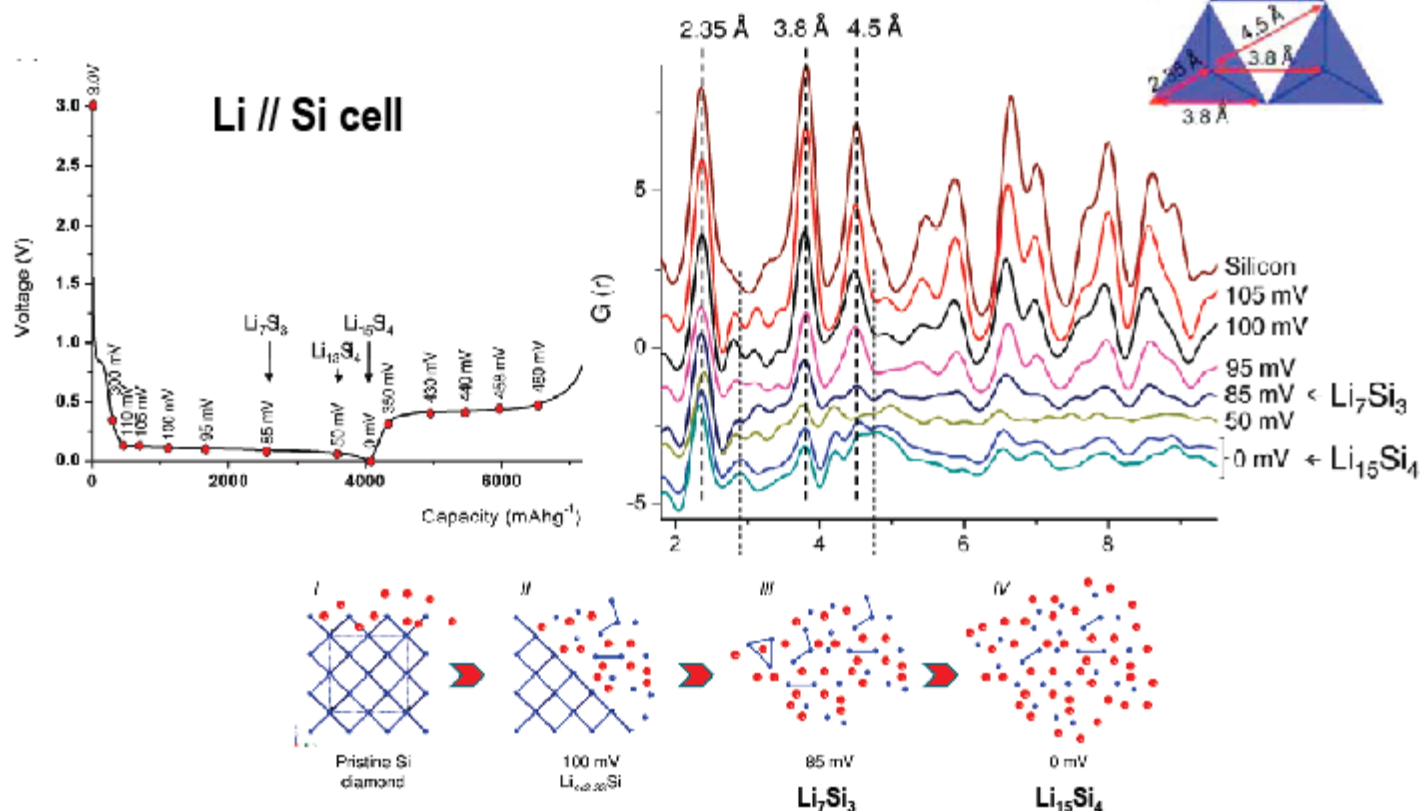


Crystal Structure of Olivine LiFePO_4



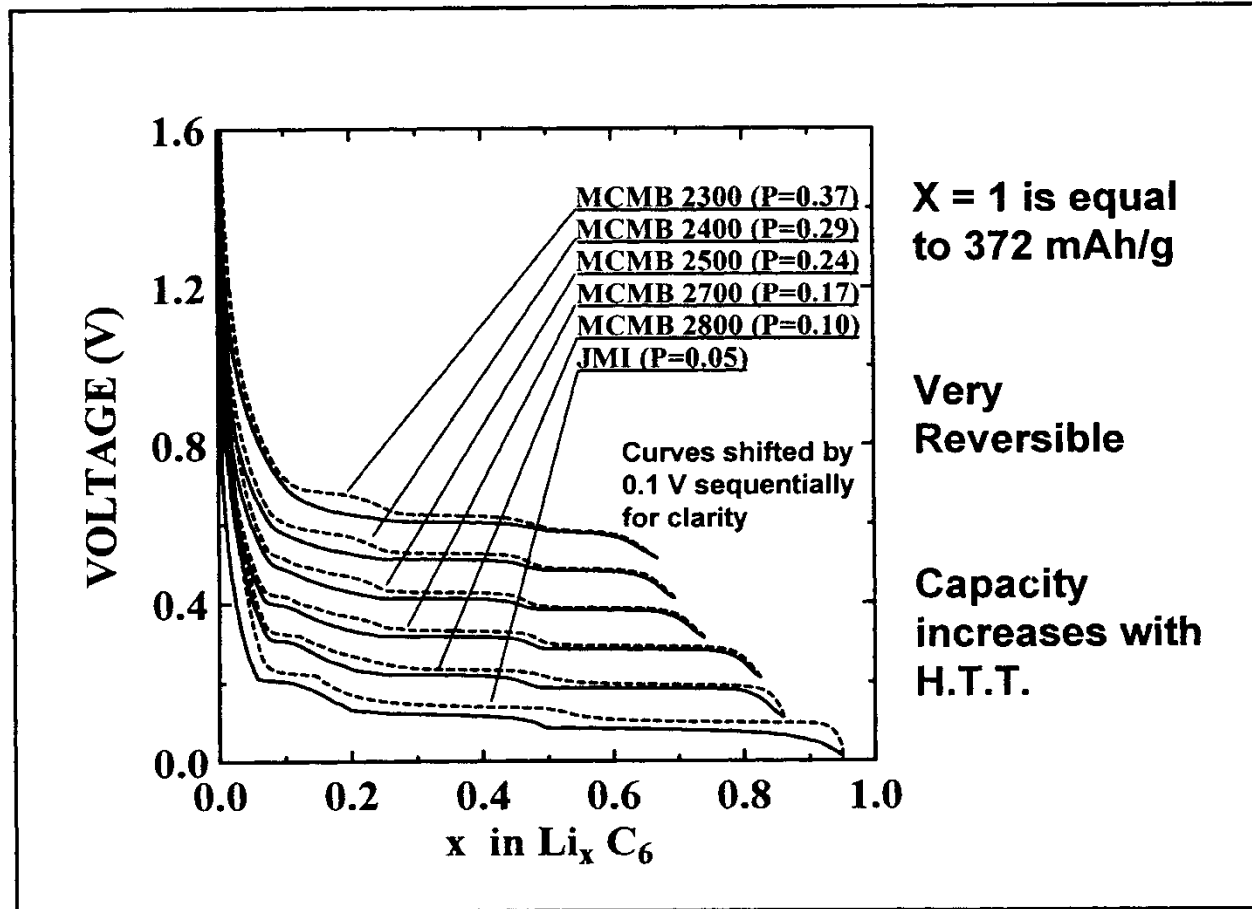
Structure Evolution of Si anode upon cycling

Silicon as Negative Electrode: Insights of PDF Analysis in the Lithium Intercalation and Deintercalation Processes

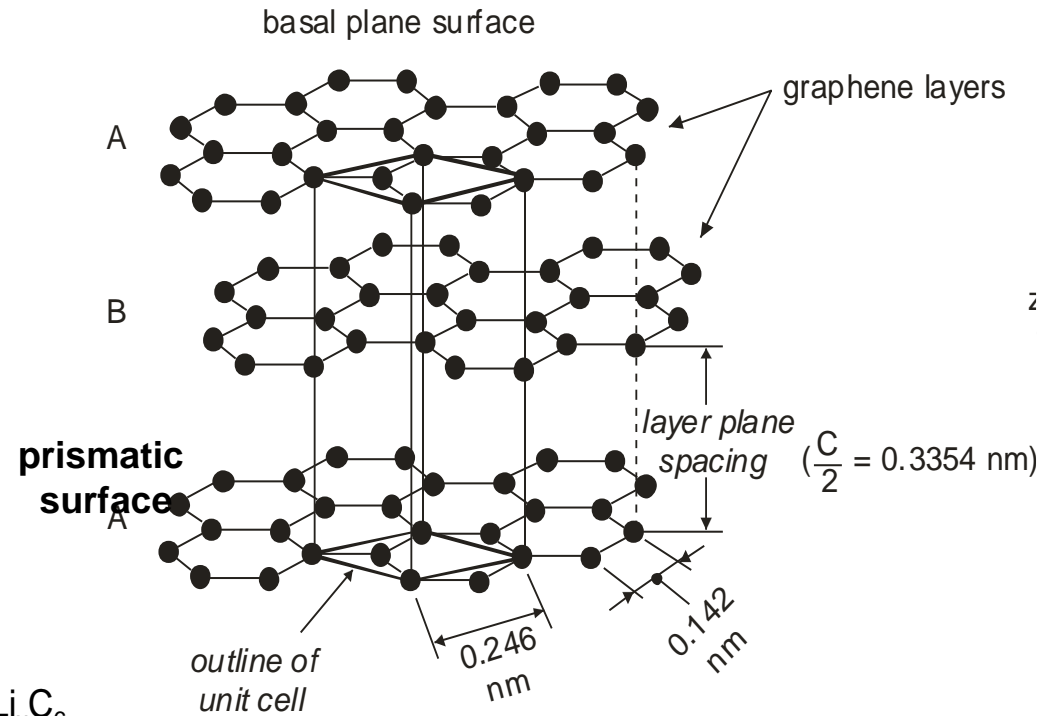
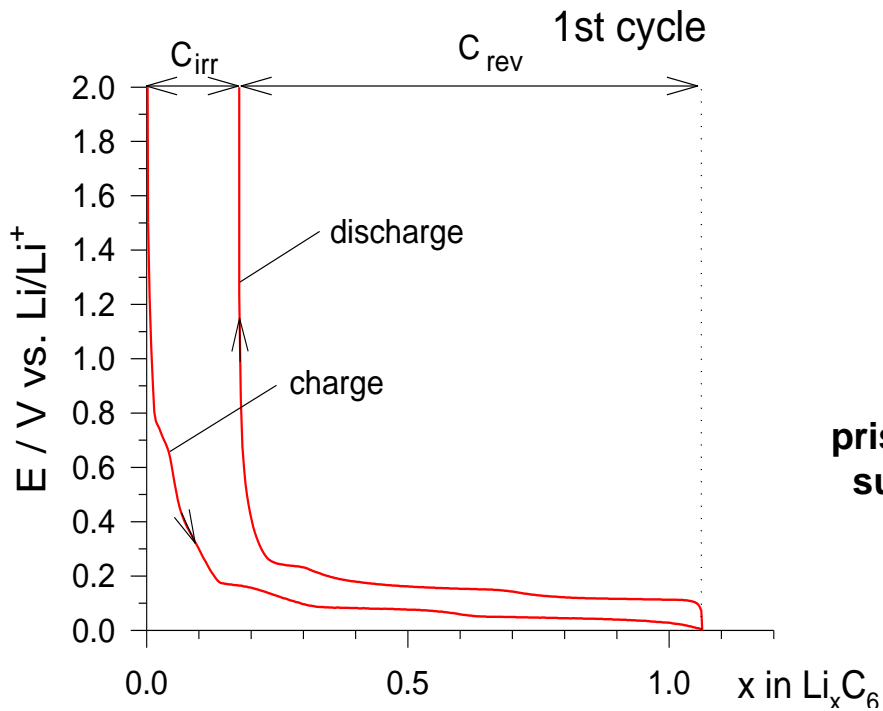


Key, Morcrette, Tarascon, Grey, *J. Am. Chem. Soc.* 2011

Carbon-MCMB



Graphitic Carbon: SEI Formation in the 1st Cycle Leads to Irreversible Capacity

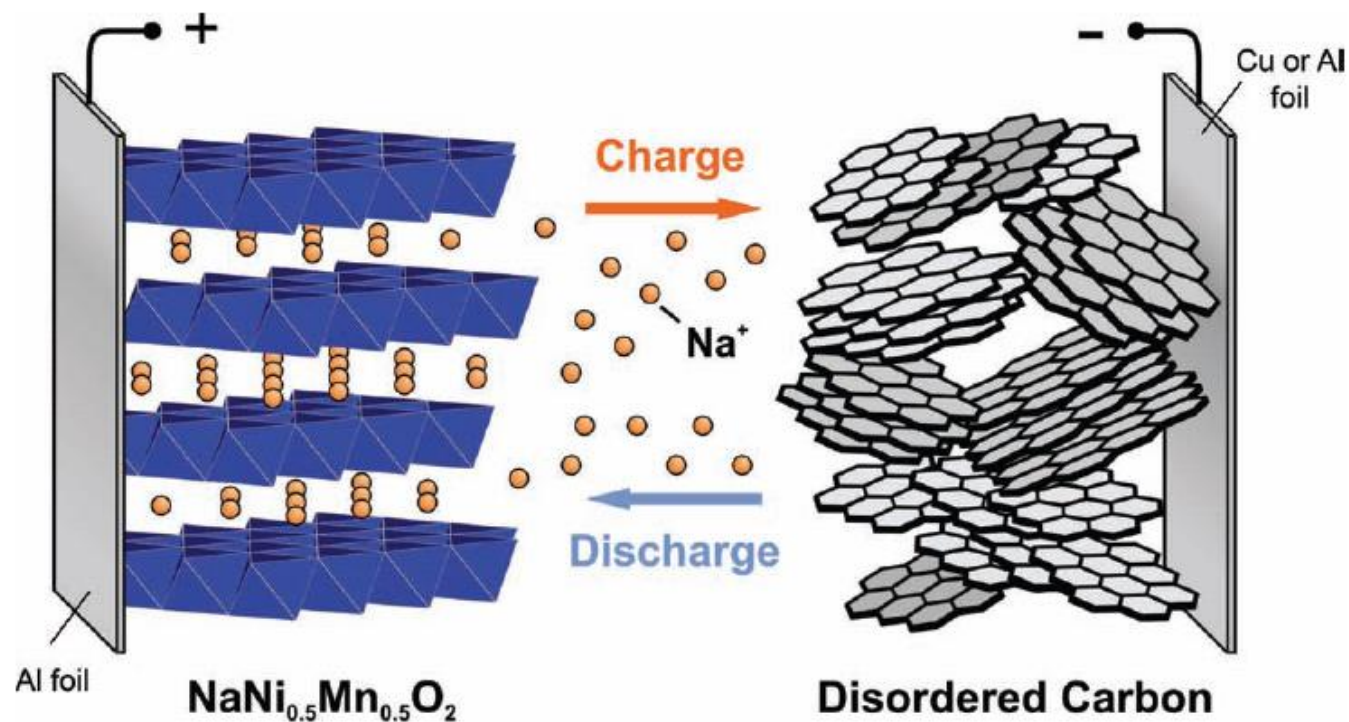


SEI formation process and SEI properties depend on:

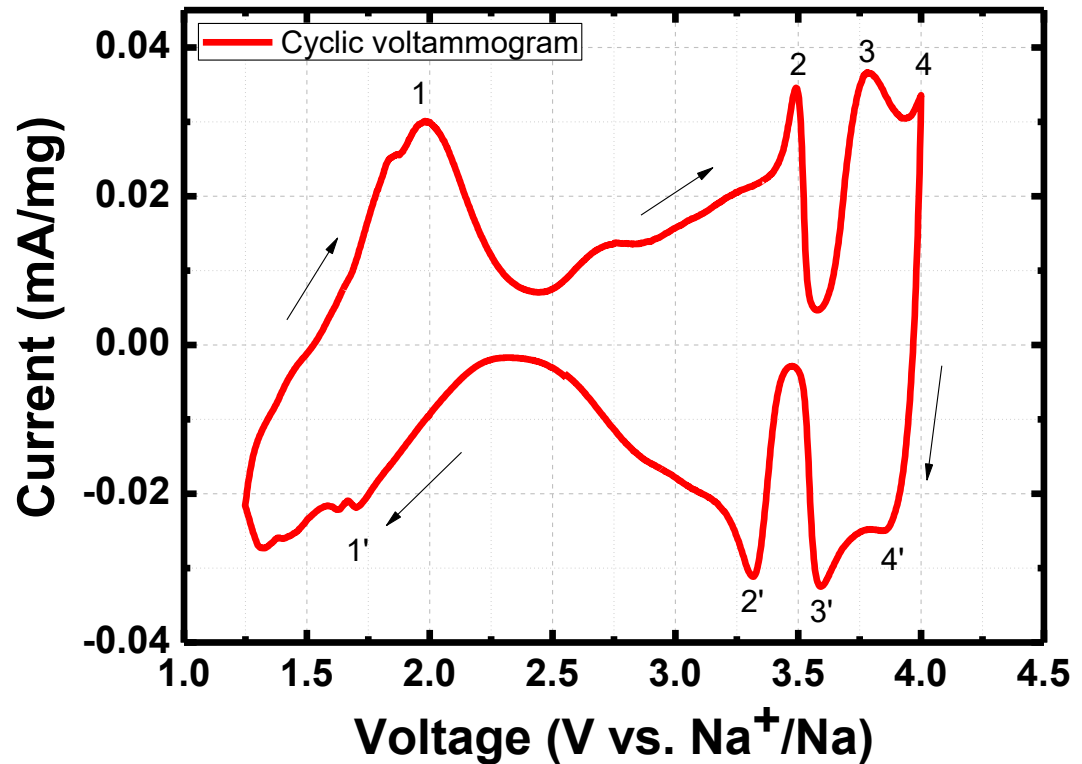
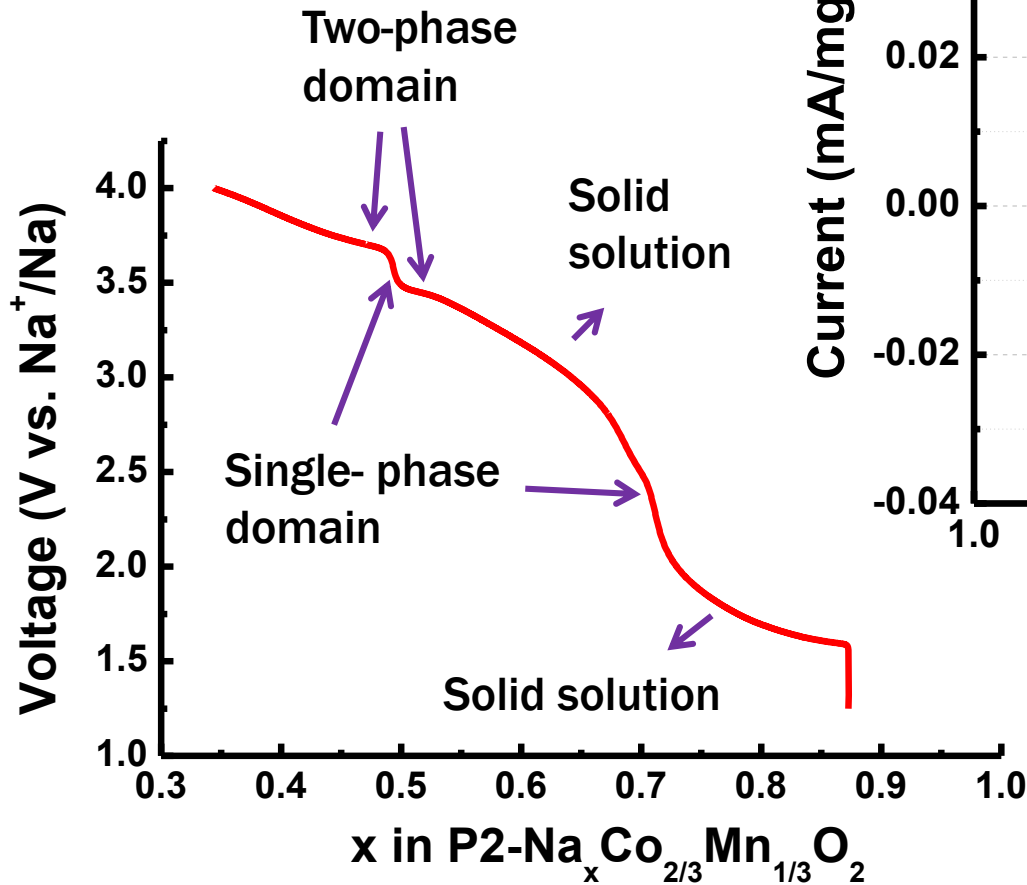
graphite material: (i) surface area, (ii) surface morphology, (iii) surface heterogeneities (basal plane and prismatic surfaces, surface groups), and (iv) graphite crystallinity (solvent co-intercalation) and electrolyte composition.

Working Principle of Li/Na-ion Battery

| Lithium | Sodium | Category |
|----------------------------|--------------------------|--|
| 0.76 | 1.06 | Cation radius (Å) |
| 6.9 g mol ⁻¹ | 23 g mol ⁻¹ | Atomic weight |
| 0 | 0.3 V | E° (vs. Li/Li ⁺) |
| \$5000/ton | \$150/ton | Cost, carbonates |
| 3829 | 1165 | Capacity (mAh g ⁻¹), metal |
| Octahedral and tetrahedral | Octahedral and prismatic | Coordination preference |



Sodium Ion Batteries



- The two single phase domain is found in $x = 2/3$ and $1/2$

Recap!