# 1.1.2 Faradaic and Nonfaradaic Processes

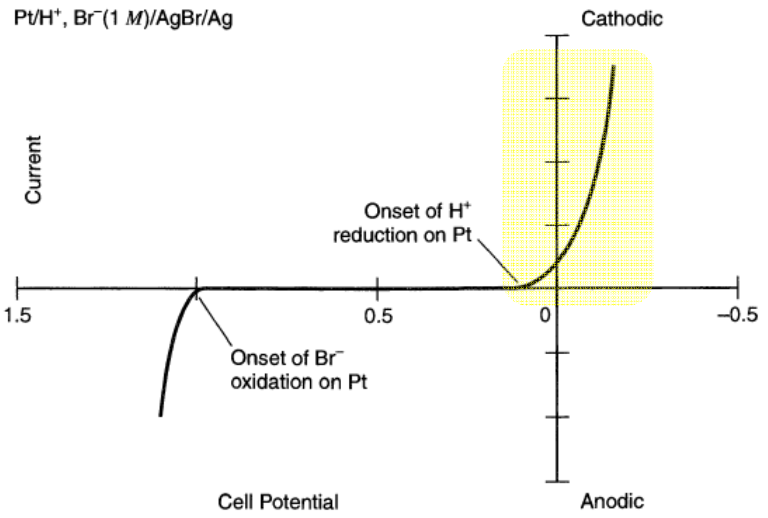
- Two types of electrochemical processes

## 1) Faradaic process

: charges (e.g., electrons) are transferred across the metal-solution interface.

➔ Electron transfer causes oxidation or reduction to occur.

➔ Since this reactions are governed by Faraday's law (i.e., the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed), they are called faradaic processes.



# 1.1.2 Faradaic and Nonfaradaic Processes

## 2) Nonfaradaic process

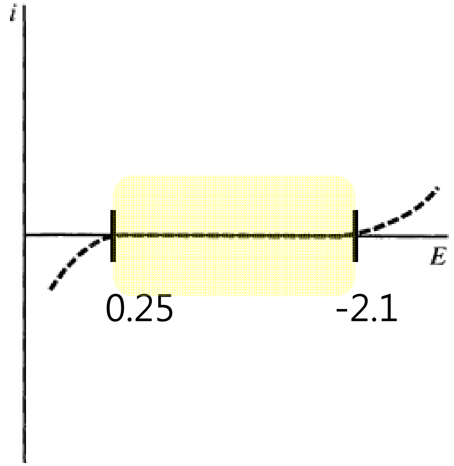
In a specific range of potentials

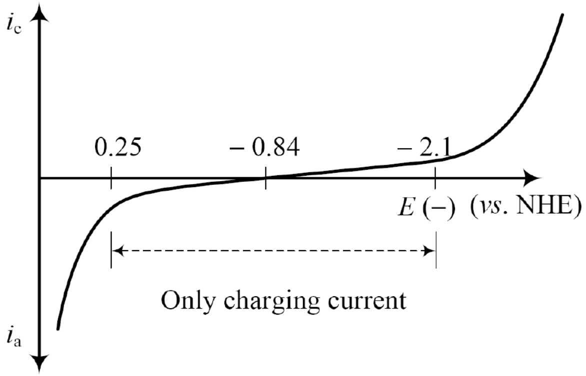
: charge-transfer reactions are thermodynamically or kinetically unfavorable

➔ no charge-transfer reactions occur

➔ However, processes such as adsorption and desorption can occur on the surface of electrodes

➔ Although charge does not cross the interface, external currents can flow (at least transiently) when the potential or solution composition changes.





➔ Nonfaradaic current: dependent on the surface area of electrodes and concentration of electrolytes

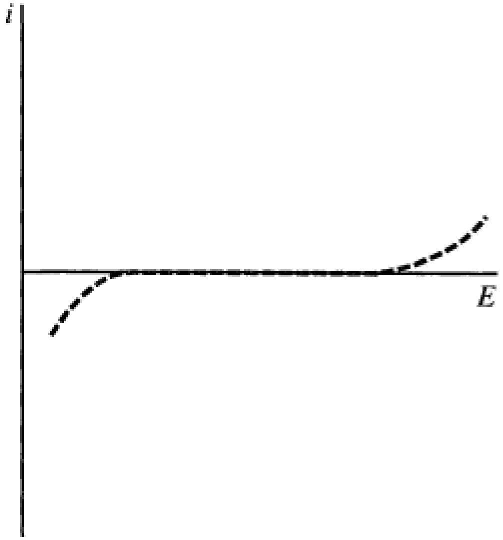
➔ Both faradaic and nonfaradaic processes can simultaneously occur when electrode reactions take place

# 1.2.1 Ideal Polarized Electrode

- Ideal polarized (or ideal polarizable) electrode (IPE)

  ➔ defined as an electrode at which no charge transfer can occur across the metal-solution interface, regardless of the potential imposed by an outside source of voltage

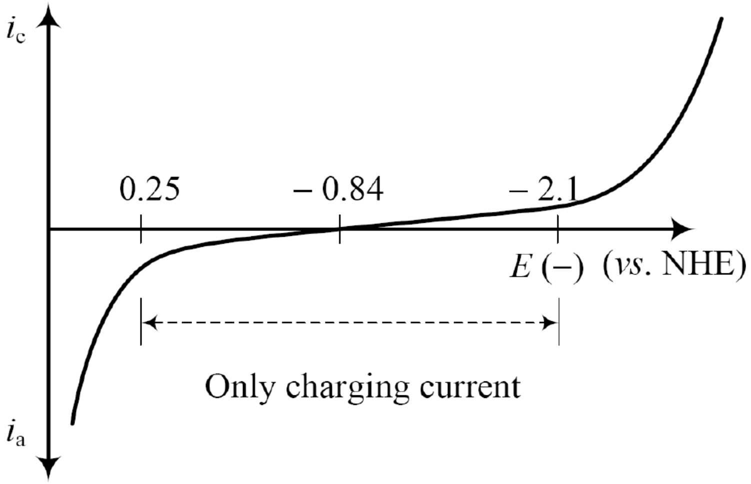
- While no real electrode can behave as an IPE over the whole potential range available in a solution, some electrode-solution systems can approach ideal polarizability over limited potential ranges



(*a*) Ideal polarizable electrode

# 1.2.1 Ideal Polarized Electrode

- For example, a mercury electrode in contact with a deaerated potassium chloride solution approaches the behavior of an IPE over a potential range about 2 V wide.



➔ At sufficiently positive potentials, the mercury can oxidize in a charge-transfer reaction:

$$\mathrm{Hg} + \mathrm{Cl}^- \rightarrow \tfrac{1}{2}\mathrm{Hg_2Cl_2} + e \qquad (\text{at} \sim +0.25\ \text{V } vs.\ \text{NHE})$$

➔ at very negative potentials $K^+$ can be reduced:

$$\mathrm{K}^+ + e \overset{\mathrm{Hg}}{\rightarrow} \mathrm{K(Hg)} \qquad (\text{at} \sim -2.1\ \text{V } vs.\ \text{NHE})$$

➔ In the potential range between these processes, the reduction of water is thermodynamically possible (-0.828 V vs. NHE), but occurs at a very low rate at a mercury surface unless quite negative potentials are reached.

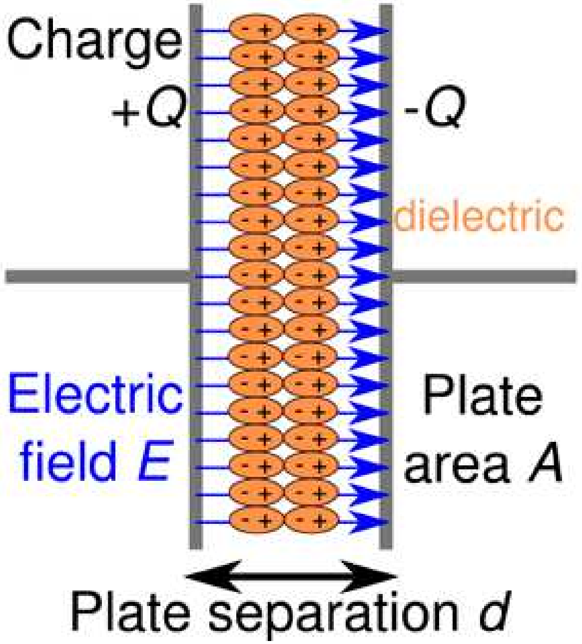
$$\mathrm{H_2O} + e \rightarrow \tfrac{1}{2}\mathrm{H_2} + \mathrm{OH}^-$$

# 1.2.2 Capacitance and Charge of an Electrode

- The behavior of the electrode-solution interface of IPE

  : analogous to that of a capacitor

  ➔ Since charge cannot cross the IPE interface when the potential across it is changed



- A capacitor is an electrical circuit element composed of two metal sheets separated by a dielectric material.

- The behavior of IPE is governed by the equation of capacitor

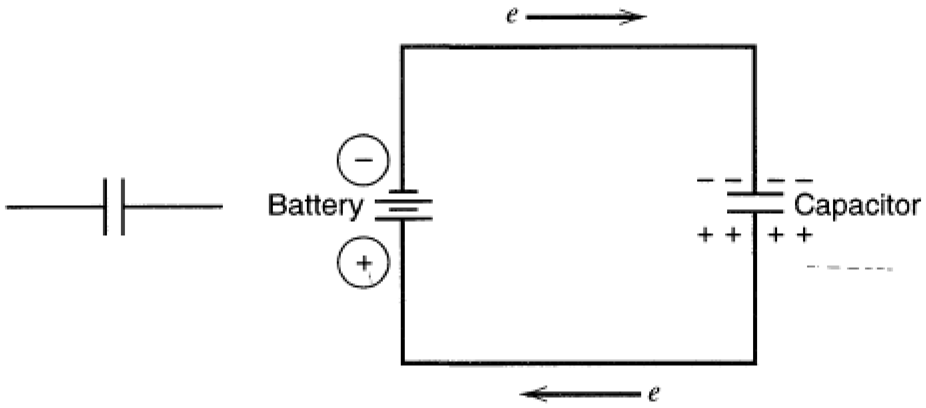
$$\frac{q}{E} = C$$

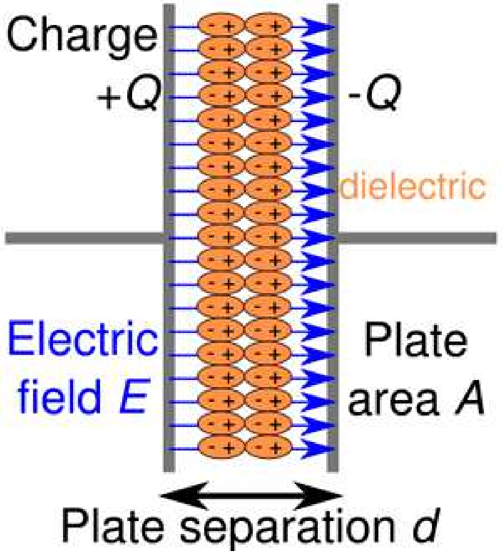
: where q is the charge stored on the capacitor (in coulombs, C), E is the potential across the capacitor (in volts, V), and C is the capacitance (in farads, F).

# 1.2.2 Capacitance and Charge of an Electrode

## Principle of a capacitor

- When a potential is applied across a capacitor, charge will accumulate on its metal plates until q satisfies the equation of q = CE
- During this charging process, a current (called the charging current) will flow.
- The charge on the capacitor consists of an excess of electrons on one plate, a deficiency of electrons on the other, and a polarized dielectric





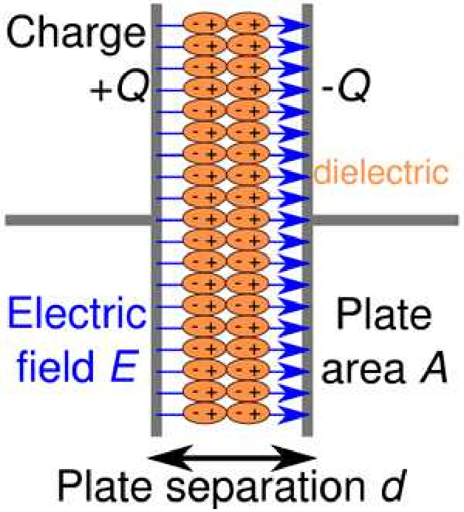
# 1.2.2 Capacitance and Charge of an Electrode

## Principle of nonfaradaic processes

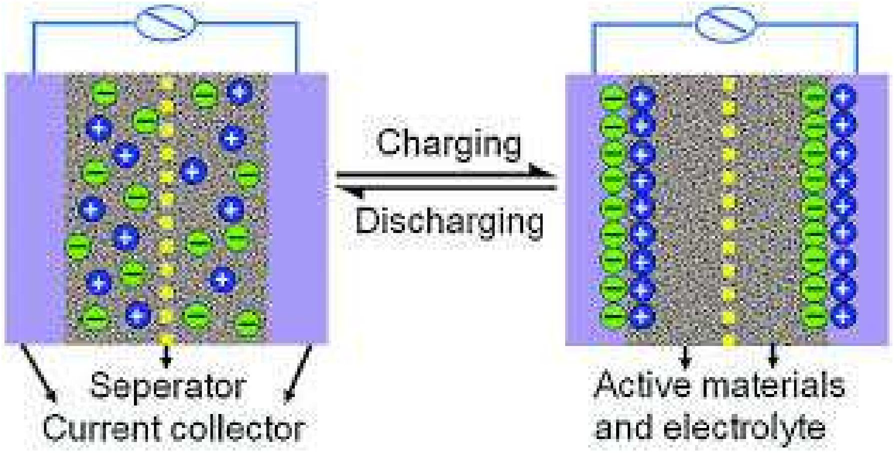
- The electrode-solution interface of nonfaradic processes behaves like a capacitor

  ➔ suggest a model of the nonfaradic processes resembling a capacitor
- Electrolytes in nonfaradic processes

  : regarded as dielectric materials in capacitors



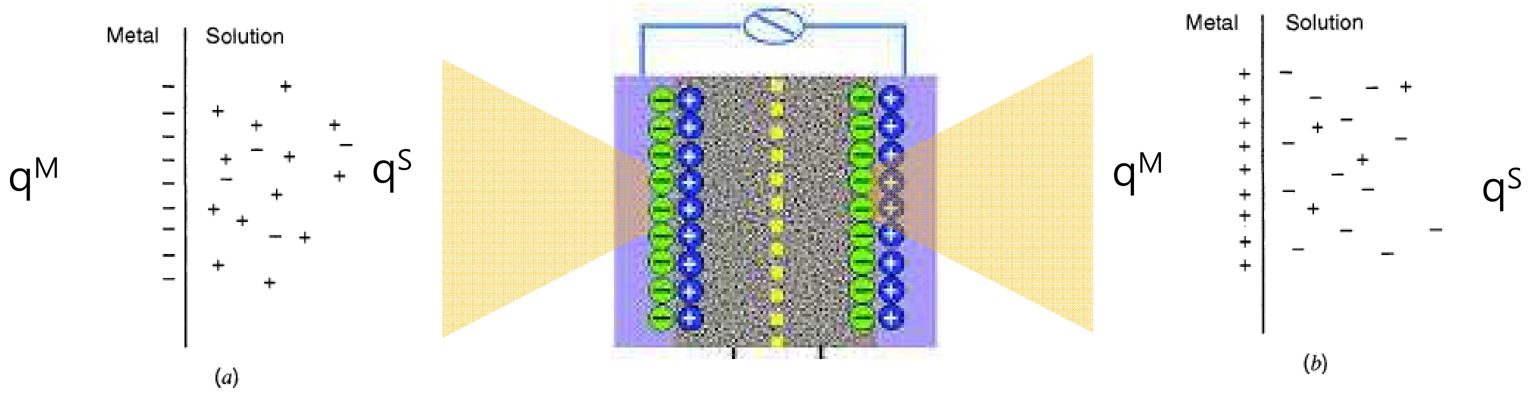
Polarization of dielectric



Ion (charge) separation

## 1.2.2 Capacitance and Charge of an Electrode

- At a given potential, there exist a charge (electron or hole) on the metal electrode, $q^M$, and a charge (ion) in the solution, $q^S$
- Whether the charge on the metal is negative or positive with respect to the solution depends on the potential across the interface and the composition of the solution.
- At all times, $q^M = -q^S$.
- The charge on the metal, $q^M$, represents an excess or deficiency of electrons and resides in a very thin layer (<0.1 Å) on the metal surface.
- The charge in solution, $q^S$, is made up of an excess of either cations or anions in the vicinity of the electrode surface.



# 1.2.2 Capacitance and Charge of an Electrode

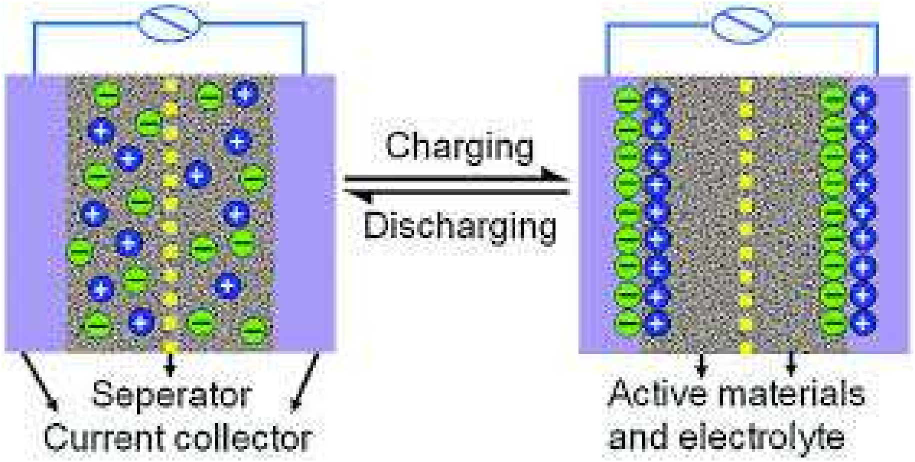
- Electrical double layer

  : the whole array of charged species and oriented dipoles existing at the metal-solution interface

- The double-layer capacitance, $C_d$, of the electrode-solution interface

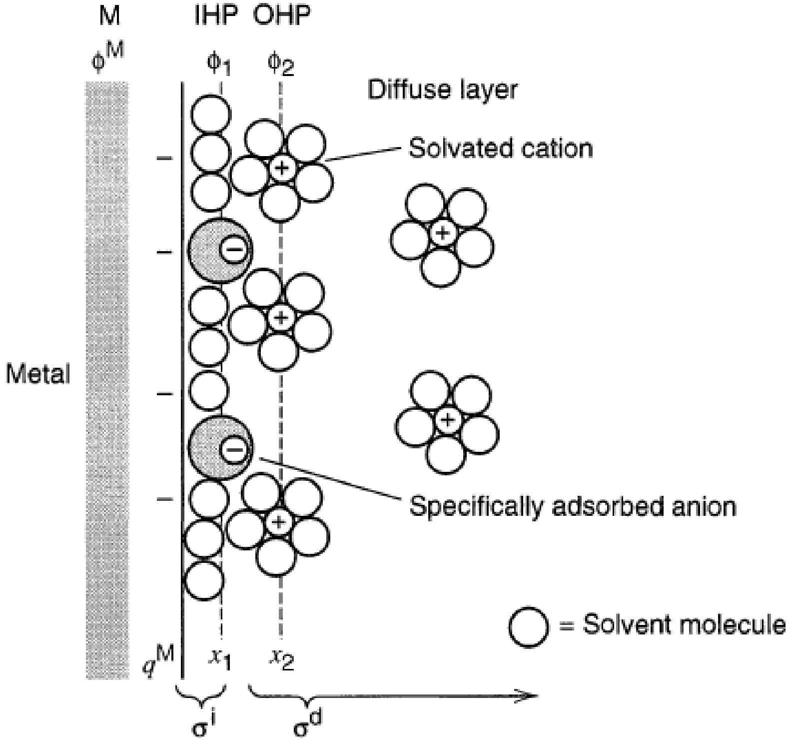
  : typically in the range of 10 to 40 μF/cm$^2$ (F=C/V)

- However, unlike real capacitors, whose capacitances are independent of the voltage across them, Q is often a function of potential

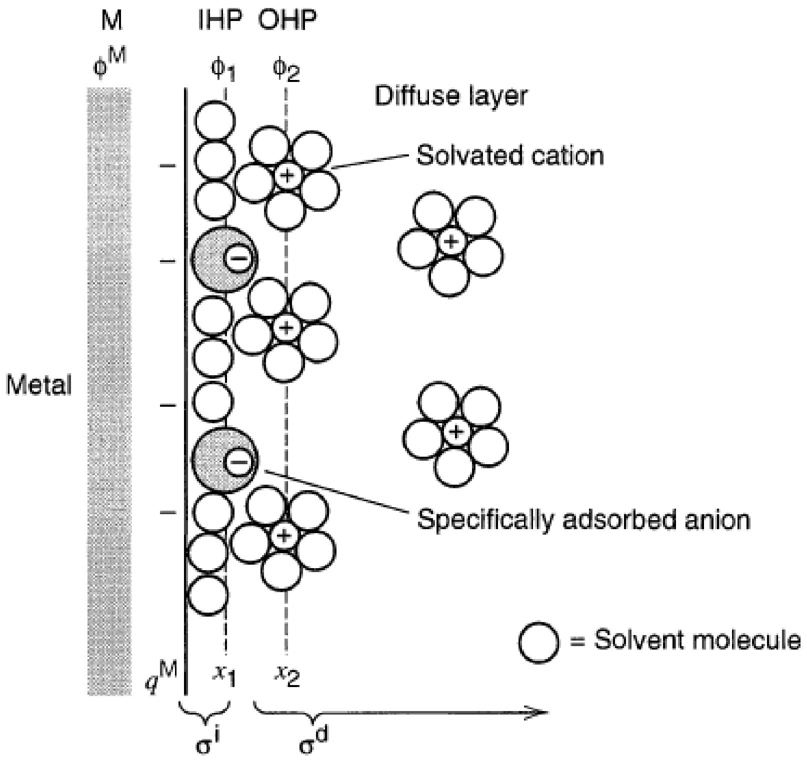


# 1.2.3 Brief Description of the Electrical Double Layer

- The solution side of the double layer
  : is thought to be made up of several "layers."
- That closest to the electrode, the inner layer, contains solvent molecules and sometimes specifically adsorbed anion with direct bonding to metal substrates (Bockris-Devanathan-Mueller model)
  ➔ This inner layer is called the compact, Helmholtz, or Stern layer.



# 1.2.3 Brief Description of the Electrical Double Layer



- The locus of the electrical centers of the specifically adsorbed ions at a distance $x_1$

  ➔ the inner Helmholtz plane (IHP)
- Solvated ions can approach the metal only to a distance $x_2$
- The locus of centers of these nearest solvated ions at a distance $x_2$

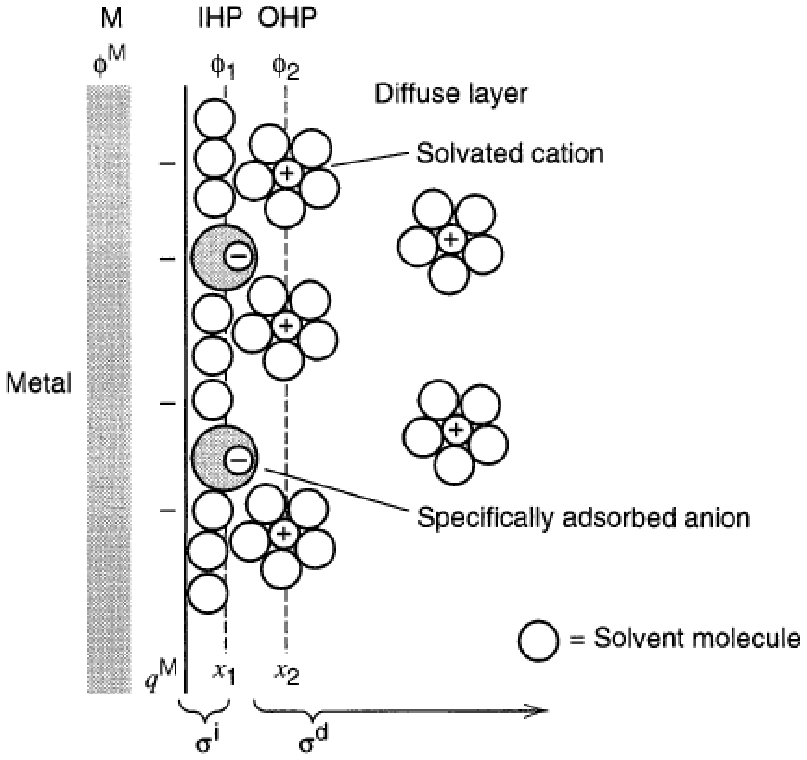
  ➔ the outer Helmholtz plane (OHP)
- Because of thermal agitation in the solution, the nonspecifically adsorbed ions are distributed from the OHP into the bulk of the solution

  ➔ the diffuse layer

# 1.2.3 Brief Description of the Electrical Double Layer

- The total charge density from specifically adsorbed ions in the inner layer  
  : $\sigma^i$ μC/cm$^2$.
- The excess charge density in the diffuse layer  
  : $\sigma^d$
- The total excess charge density on the solution side of the double layer, $\sigma^S$, is given by

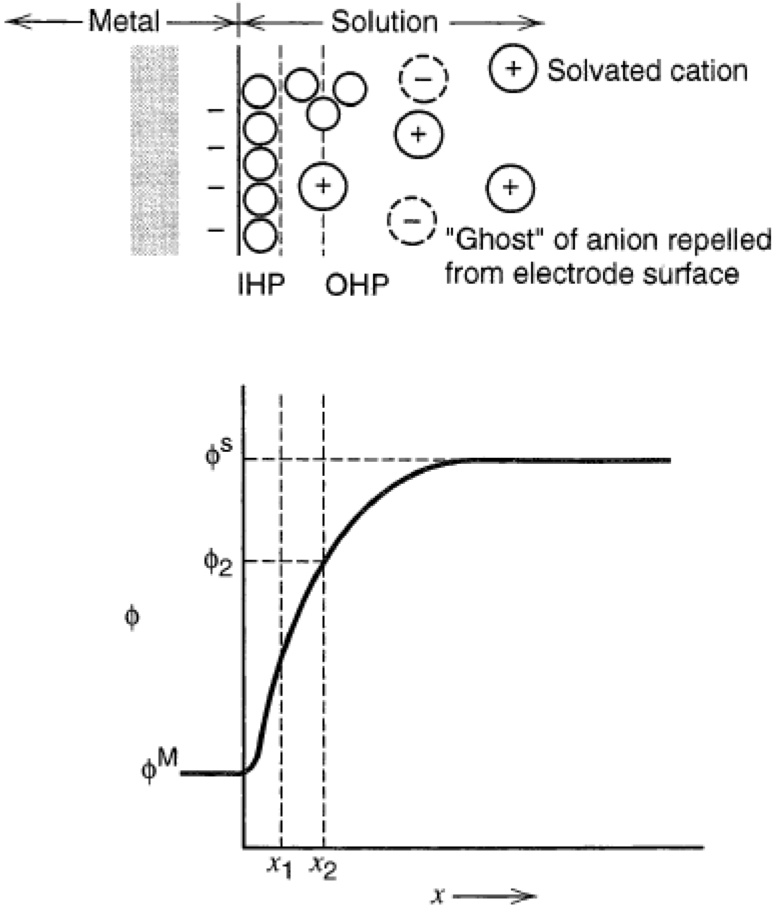
$$\boxed{\sigma^S = \sigma^i + \sigma^d = -\sigma^M}$$



- The thickness of the diffuse layer depends on the total ionic concentration in the solution
- For concentrations greater than $10^{-2}$ *M*, the thickness is less than ~100 Å.

# 1.2.3 Brief Description of the Electrical Double Layer

- The potential profile across the double-layer region



# 1.3 Faradaic Processes: input vs. output

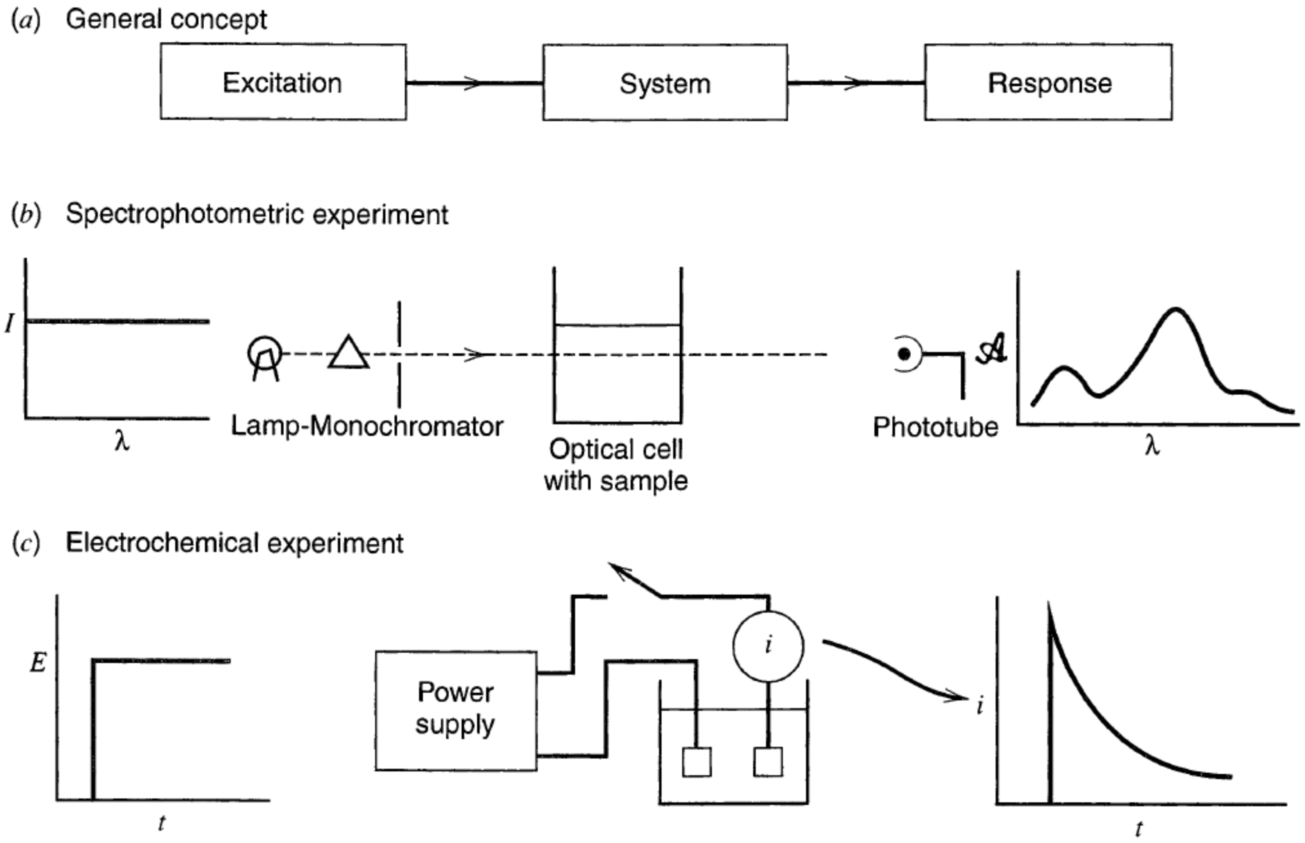


**Figure 1.3.3** (*a*) General principle of studying a system by application of an excitation (or perturbation) and observation of response. (*b*) In a spectrophotometric experiment, the excitation is light of different wavelengths ($\lambda$), and the response is the absorbance ($\mathscr{A}$) curve. (*c*) In an electrochemical (potential step) experiment, the excitation is the application of a potential step, and the response is the observed *i*-*t* curve.

# 1.3 Faradaic Processes: variables

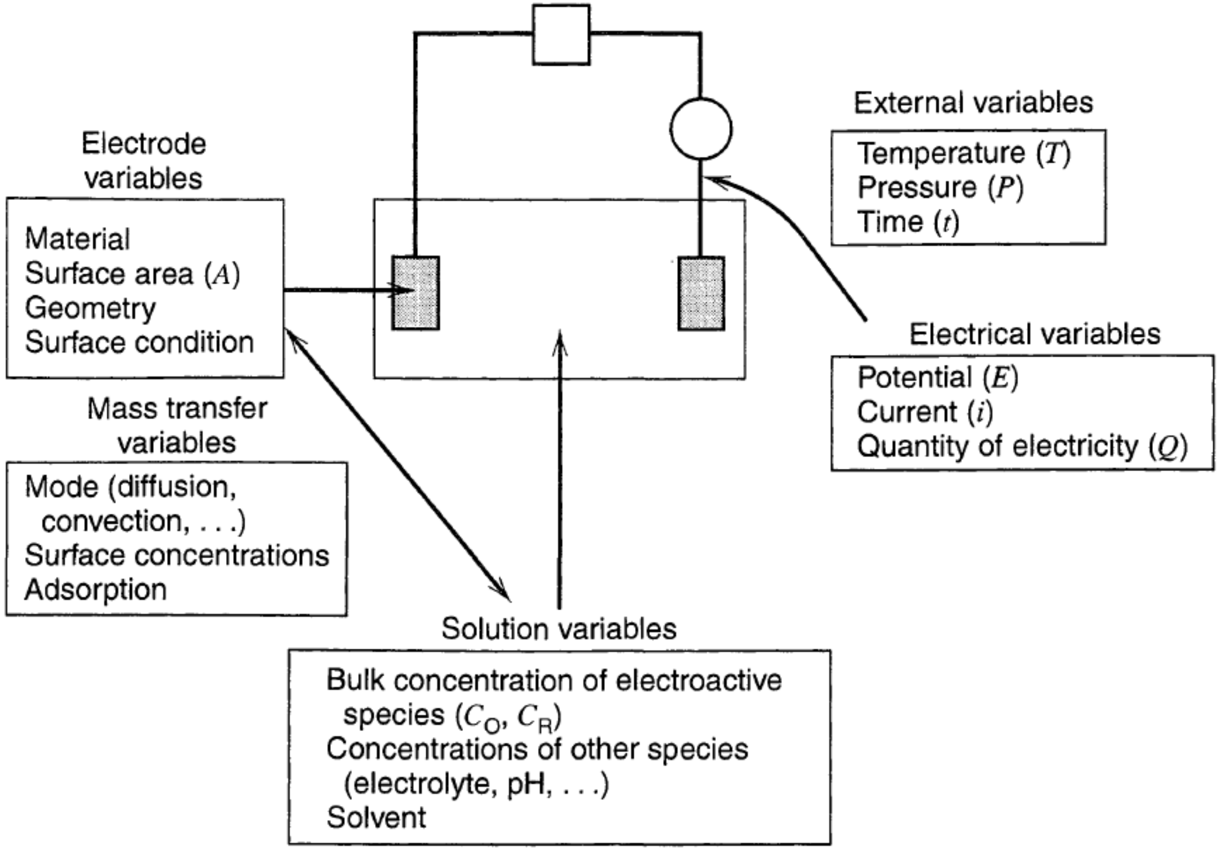


**Figure 1.3.2** Variables affecting the rate of an electrode reaction.

## 1.2.4 Double-Layer Capacitance and Charging Current in Electrochemical Measurements

- Consider a cell consisting of an IPE and an ideal reversible electrode (Hg/$K^+$,$Cl^-$/SCE)

  : IPE - mercury electrode in a potassium chloride solution

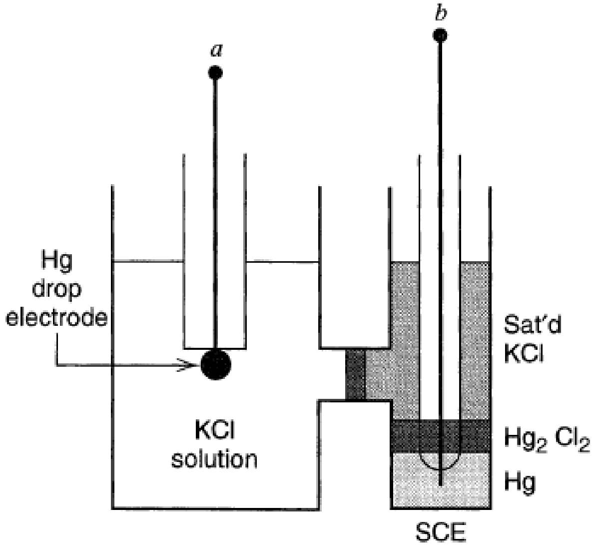
  : Reference - SCE.

- This cell can be described by an electrical circuit with a resistor, $R_s$, and capacitors, $C_d$ and $C_{SCE}$

  : $R_s$ - representing the solution resistance

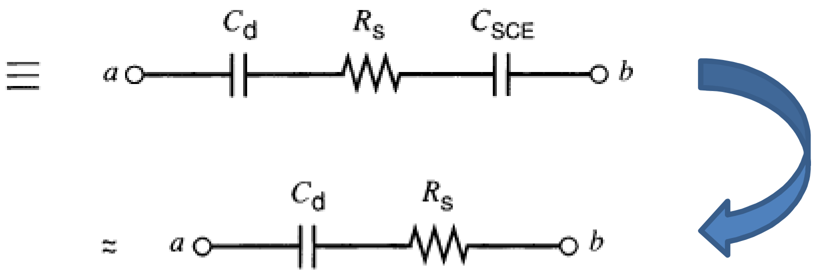
  : $C_d$ - representing the double layer at the Hg/$K^+$,$Cl^-$ interface

  : $C_{SCE}$ - representing the capacitance at the SCE



Two-electrode cell with an ideal polarized mercury drop electrode and an SCE

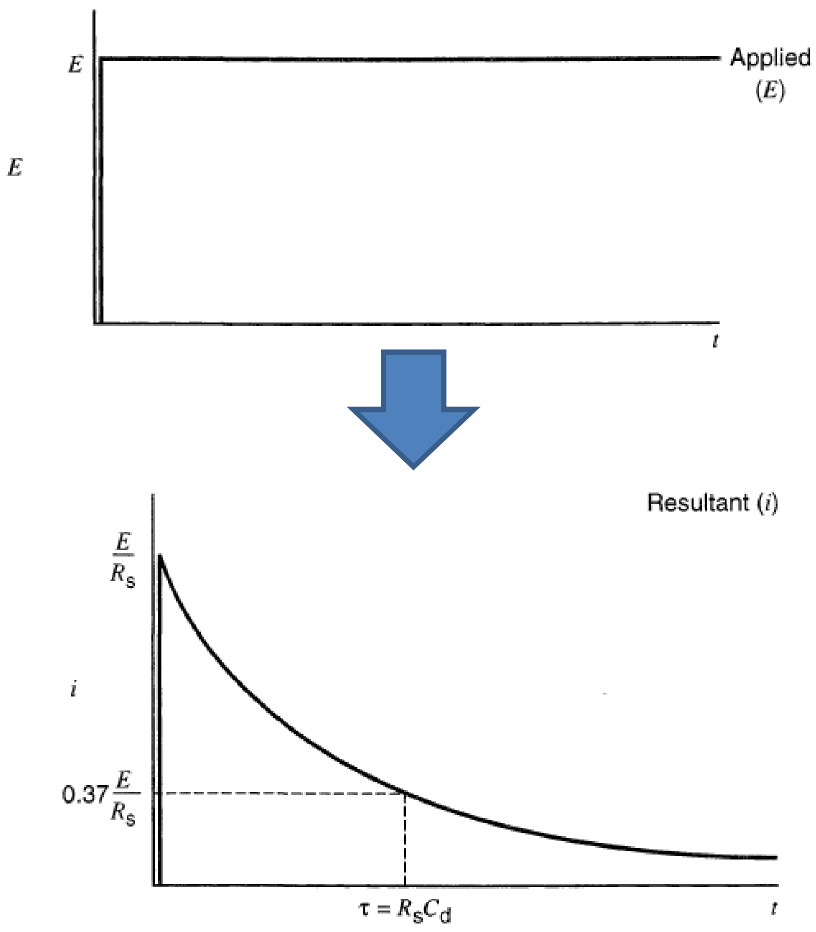
Representation of the cell in terms of linear circuit elements



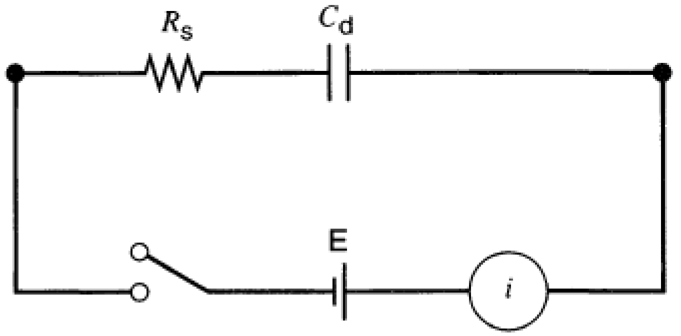
$C_d << C_{SCE}$

## 1.2.4 Double-Layer Capacitance and Charging Current in Electrochemical Measurements

### (a) Voltage (or Potential) Step



Current transient (i vs. t) resulting from a potential step experiment



Potential step experiment for an RC circuit.

➔ The similar current transient of a potential step to the RC circuit problem will be obtained for that of the IPE

# 1.2.4 Double-Layer Capacitance and Charging Current in Electrochemical Measurements

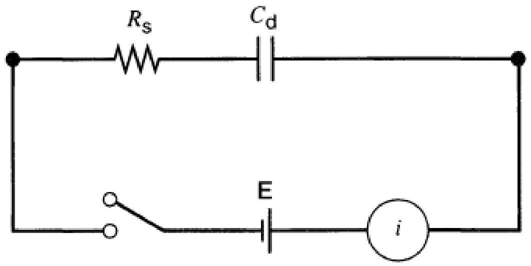
- Let us derive the governing equation of the current transient, i, with time, t, when applying a potential step of magnitude E

1) This derivation is started from the general equation for the charge, q, on a capacitor as a function of the voltage across it, $E_C$

$$q = C_d E_C$$

2) At any time the sum of the voltages, $E_R$ and $E_C$, across the resistor and the capacitor, respectively, must equal the applied voltage; hence

$$E = E_R + E_C = iR_s + \frac{q}{C_d}$$



## 1.2.4 Double-Layer Capacitance and Charging Current in Electrochemical Measurements

3) Noting that i = dq/dt and rearranging yields

$$E = E_{\mathrm{R}} + E_{\mathrm{C}} = iR_{\mathrm{s}} + \frac{q}{C_{\mathrm{d}}} \quad \Rightarrow \quad \frac{dq}{dt} = \frac{-q}{R_{\mathrm{s}}C_{\mathrm{d}}} + \frac{E}{R_{\mathrm{s}}}$$

4) When we integrate,

: assuming that the capacitor is initially uncharged (q = 0 at t = 0),

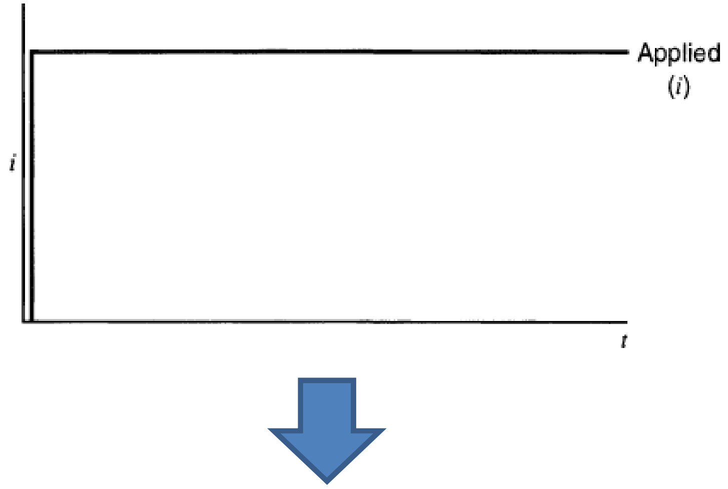
➔ then the solution is

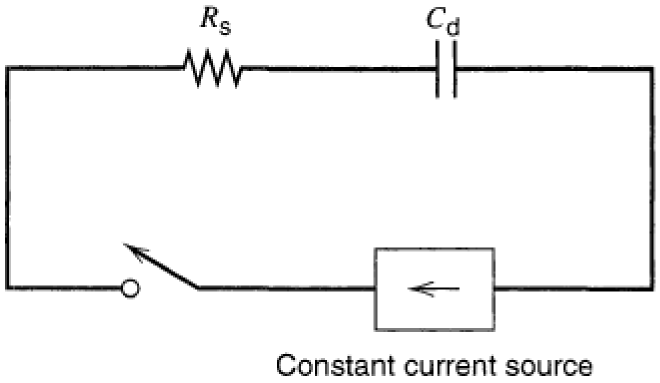
$$q = EC_{\mathrm{d}}[1 - e^{-t/R_{\mathrm{s}}C_{\mathrm{d}}}] \quad \xrightarrow[\text{by differentiating}]{} \quad \boxed{i = \frac{E}{R_{\mathrm{s}}} e^{-t/R_{\mathrm{s}}C_{\mathrm{d}}}}$$

- Hence, for a potential step input, there is an exponentially decaying current having a time constant, $\tau = R_s C_d$
- The current for charging the double-layer capacitance drops to 37% of its initial value at $t = \tau$, and to 5% of its initial value at $t = 3\tau$.

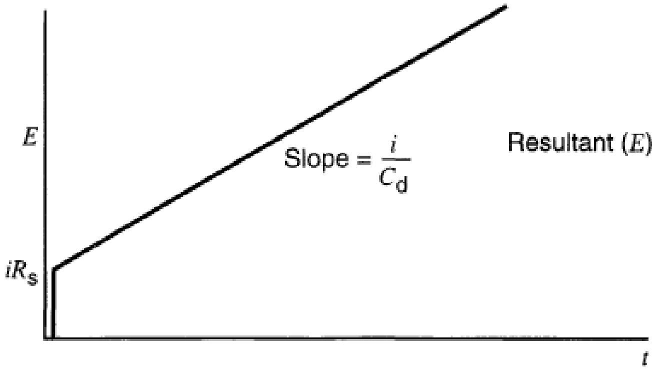
# 1.2.4 Double-Layer Capacitance and Charging Current in Electrochemical Measurements

## (b) Current Step





Current step experiment for an RC circuit.



E-t behavior resulting from a current step experiment

➔ The similar voltage behavior of a current step to the RC circuit problem will be obtained for that of the IPE

## 1.2.4 Double-Layer Capacitance and Charging Current in Electrochemical Measurements

- Let us derive the governing equation of the voltage behavior, E, with time, t, when applying a current step of magnitude i

1) When the $R_sC_d$ circuit is charged by a constant current, then the sum of the voltages, $E_R$ and $E_C$, across the resistor and the capacitor, respectively, must equal the total voltage

$$E = E_R + E_C = iR_s + \frac{q}{C_d}$$

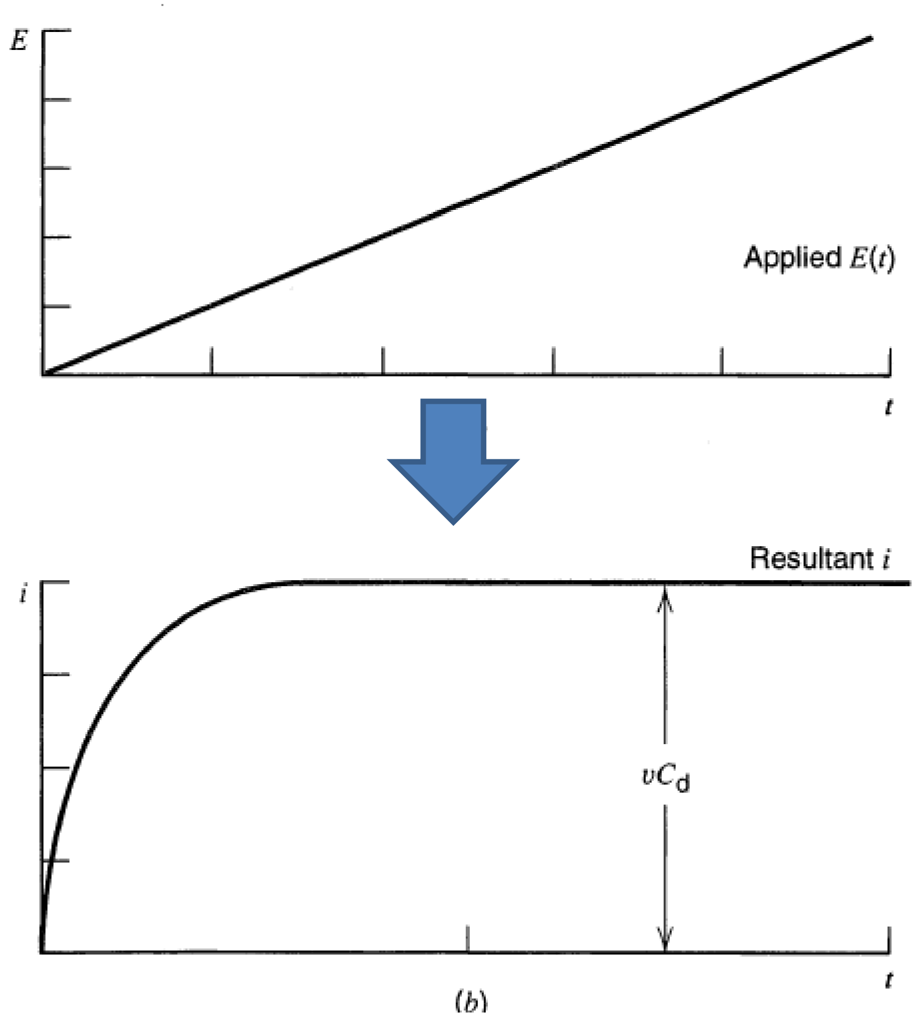
2) Since $q = \int i dt$, and i is a constant,

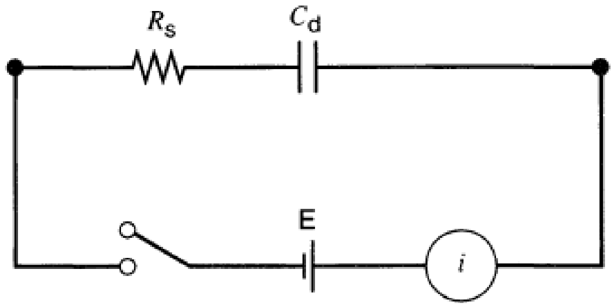
$$E = iR_s + \frac{i}{C_d}\int_0^t dt \Rightarrow \boxed{E = i(R_s + t/C_d)}$$

➔ Hence, the potential increases linearly with time for a current step

## 1.2.4 Double-Layer Capacitance and Charging Current in Electrochemical Measurements

### (c) Voltage Ramp (or Potential Sweep)





Current-time behavior resulting from a linear potential sweep applied to an *RC* circuit.

- A voltage ramp or linear potential sweep
: a potential increases linearly with time

## 1.2.4 Double-Layer Capacitance and Charging Current in Electrochemical Measurements

- Let us derive the governing equation of the current transient, i, with time, t, when a potential increases linearly with time starting at some initial value (here assumed to be zero) at a sweep rate $\upsilon$ (in V $s^{-1}$)

$$E = vt$$

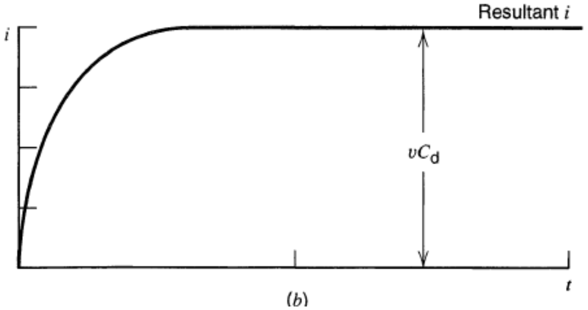
1) If such a ramp is applied to the $R_sC_d$ circuit, the following equation still applies; hence

$$E = E_R + E_C = iR_s + \frac{q}{C_d}$$

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

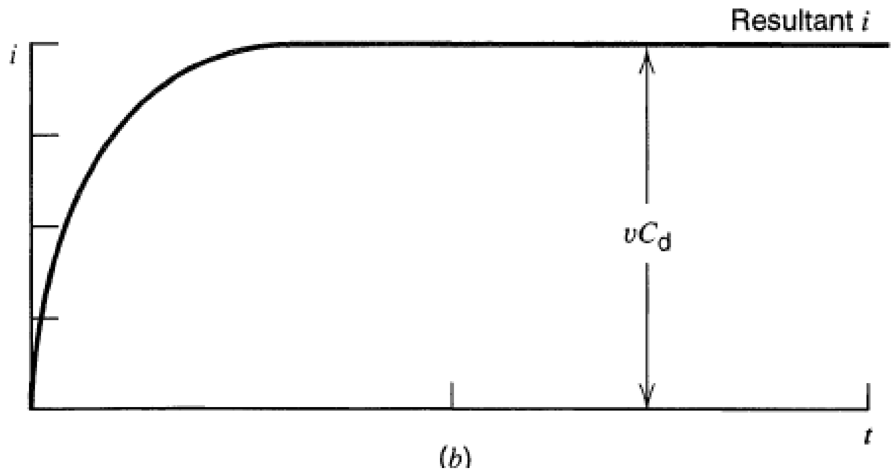
2) If q = 0 at t = 0,

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



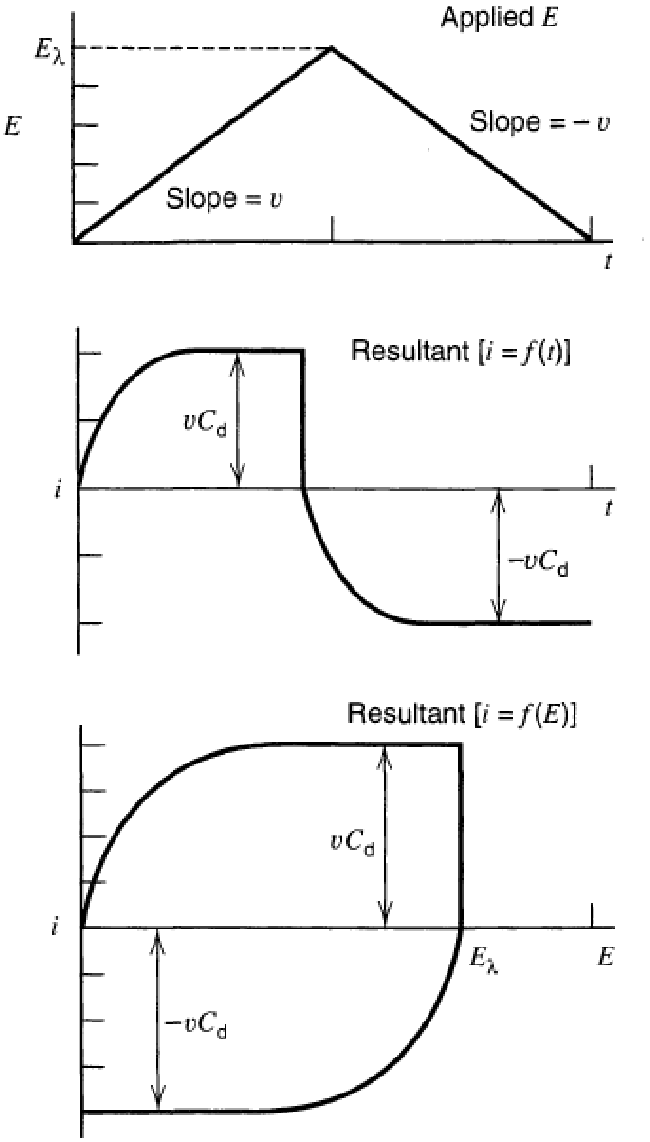
## 1.2.4 Double-Layer Capacitance and Charging Current in Electrochemical Measurements

- The current rises from zero as the scan starts and attains a steady-state value, $\upsilon C_d$
- This steady-state current can then be used to estimate $C_d$ because $\upsilon$ is known



$$i = \upsilon C_d \left[1 - \exp(-t/R_s C_d)\right]$$

# 1.2.4 Double-Layer Capacitance and Charging Current in Electrochemical Measurements



- Current-time and current-potential plots resulting from a cyclic linear potential sweep (or triangular wave) applied to an RC circuit

➔ If one instead applies a triangular wave (i.e., a ramp whose sweep rate switches from $\upsilon$ to $-\upsilon$ at some potential, $E_\lambda$), then the steady-state current changes from $\upsilon C_d$ during the forward (increasing E) scan to $-\upsilon C_d$ during the reverse (decreasing E) scan.

## 1.2.4 Double-Layer Capacitance and Charging Current in Electrochemical Measurements

Note:

- $C_d$ is generally a function of potential for nonfaradaic processes
- The approximate results can be obtained using an "average" $C_d$ over the potential range.
- The proposed model in terms of circuit elements is strictly accurate only for experiments where the overall cell potential does not change very much.

# 1.3.1 Electrochemical Cells—Types and Definitions

- Two types of Electrochemical cells in which faradaic currents

1) Galvanic cell

→ Reactions occur spontaneously at the electrodes when they are connected externally by a conductor

→ These cells are often employed in converting chemical energy into electrical energy.

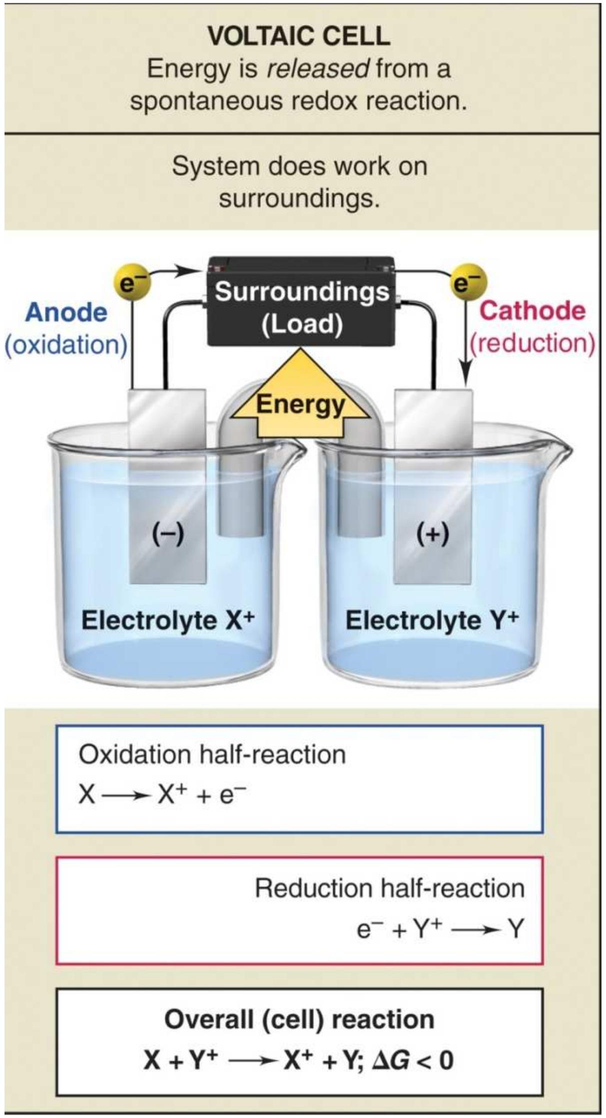
→ Galvanic cells of commercial importance include primary batteries and fuel cells

2) Electrolytic cell

→ Reactions are driven by the imposition of an external voltage greater than the open-circuit potential of the cell

→ Electroplating, production of chlorine, charging process of rechargeable batteries

# 1.3.1 Electrochemical Cells—Types and Definitions

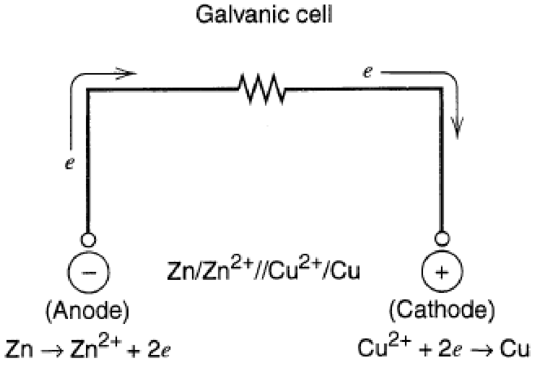

**VOLTAIC CELL**
Energy is *released* from a spontaneous redox reaction.

System does work on surroundings.

Oxidation half-reaction
$X \longrightarrow X^+ + e^-$

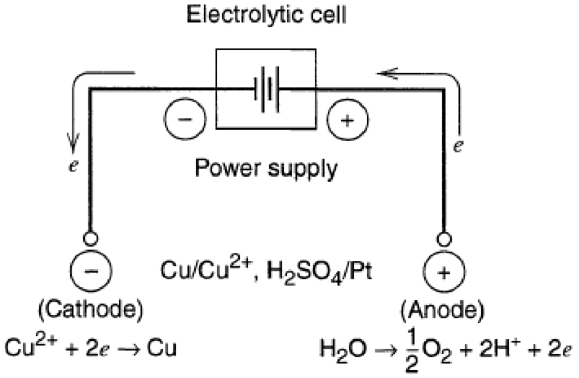
Reduction half-reaction
$e^- + Y^+ \longrightarrow Y$

**Overall (cell) reaction**
$\mathbf{X + Y^+ \longrightarrow X^+ + Y;\ \Delta G < 0}$

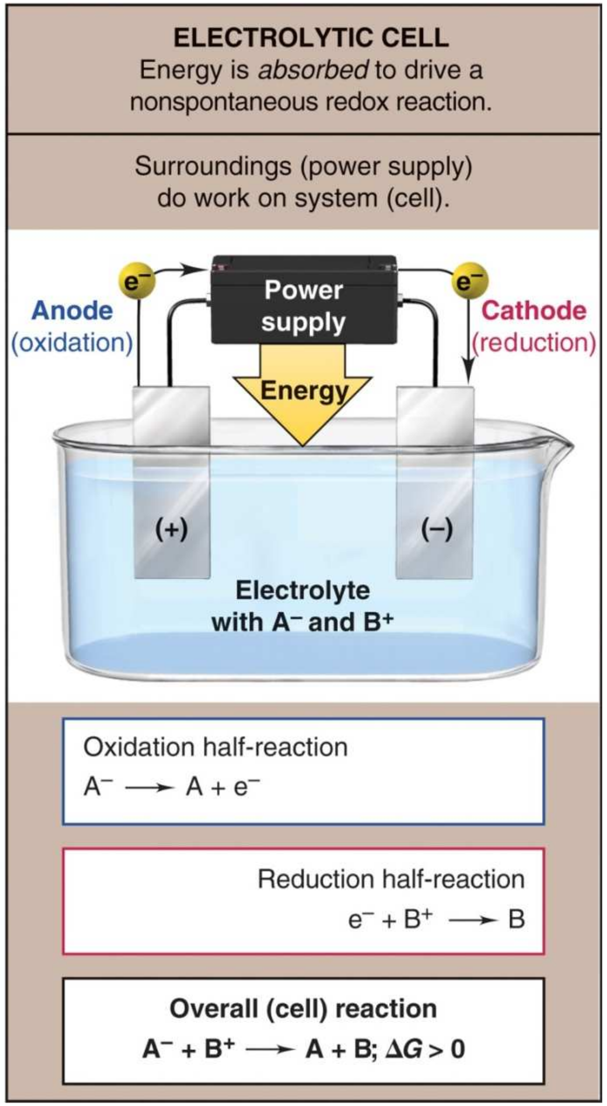


(*a*)

**Luigi Galvani**
**Alessandro Volta**



(*b*)


**ELECTROLYTIC CELL**
Energy is *absorbed* to drive a nonspontaneous redox reaction.

Surroundings (power supply) do work on system (cell).

Oxidation half-reaction
$A^- \longrightarrow A + e^-$

Reduction half-reaction
$e^- + B^+ \longrightarrow B$

**Overall (cell) reaction**
$\mathbf{A^- + B^+ \longrightarrow A + B;\ \Delta G > 0}$

# Cathode vs. Anode

- Cathode

: the electrode at which reductions occur

- Anode

: the electrode at which oxidations occur the anode.

- Cathodic current

: a current in which electrons cross the interface from the electrode to a species in solution

- Anodic current

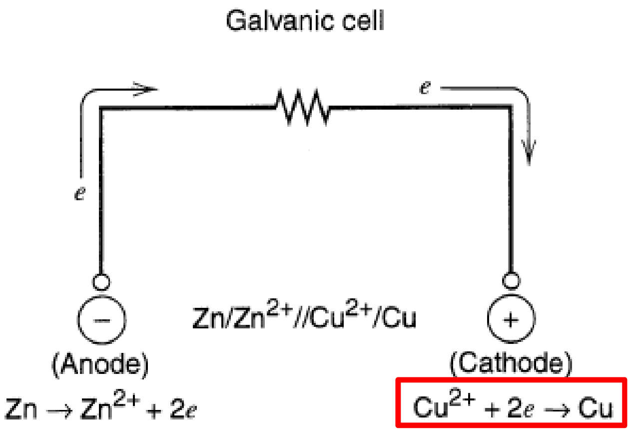
: a current in which electron flow from a solution species into the electrode

# 1.3 Faradaic Processes

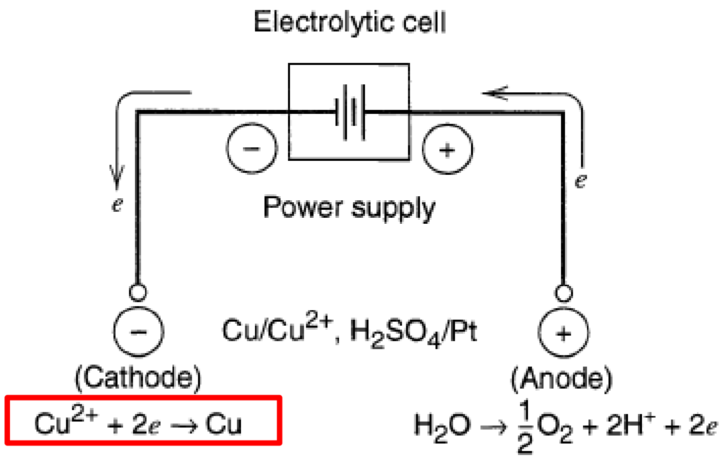
- In an electrolytic cell, the cathode is negative with respect to the anode; but in a galvanic cell, the cathode is positive with respect to the anode

- Note: we should not say, "The potential shifted in a cathodic direction," when what is meant is, "The potential shifted in a negative direction."

➔ The terms anodic and cathodic refer to electron flow or current direction, not to potential.



(a)

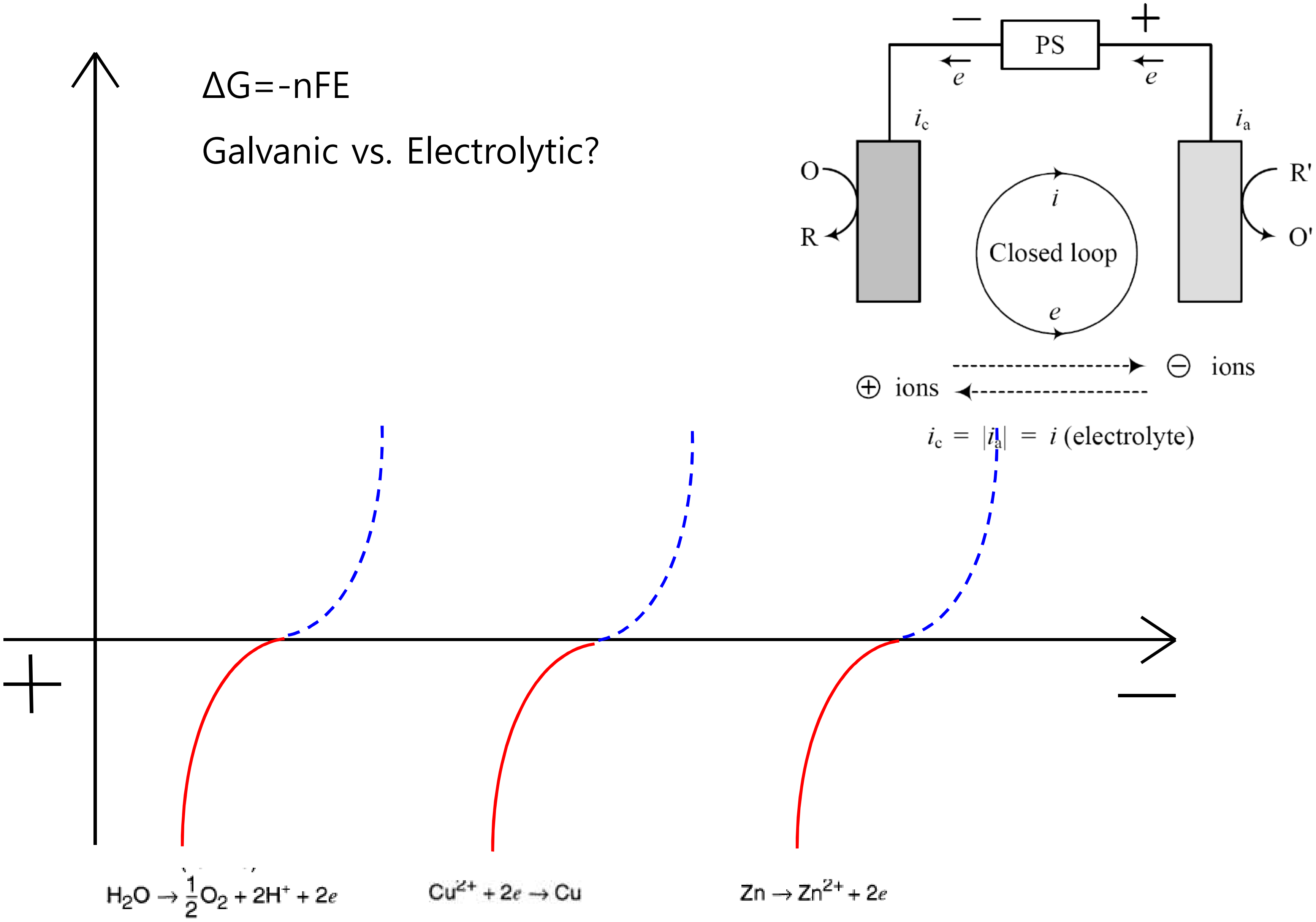


(b)

# Current passes through "closed loop"

$\Delta G = -nFE$

Galvanic vs. Electrolytic?



# 1.3 Ideal nonpolarizable electrode

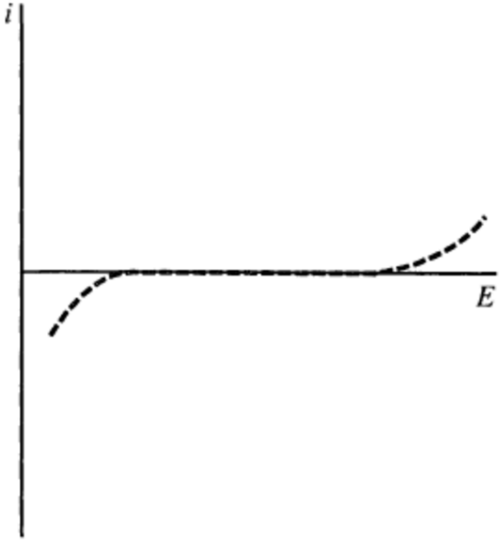
- Ideal nonpolarizable electrode (or ideal depolarized electrode)

➔ an electrode whose potential does not change upon passage of current

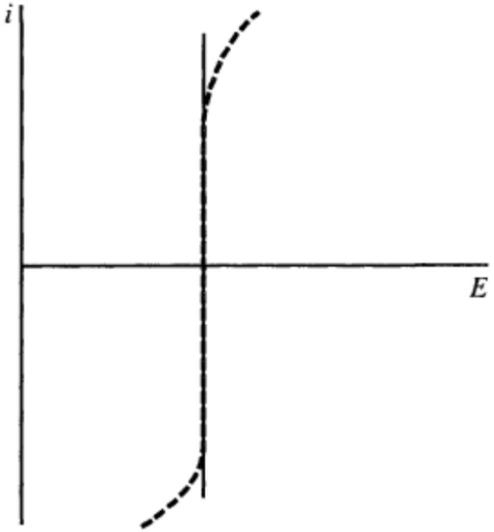
➔ an electrode of fixed potential.

- Ideal polarizable electrode ➔ a very large change in potential upon the passage of an infinitesimal current

- Ideal nonpolarizable electrode ➔ no change in potential upon the passage of an substantial current

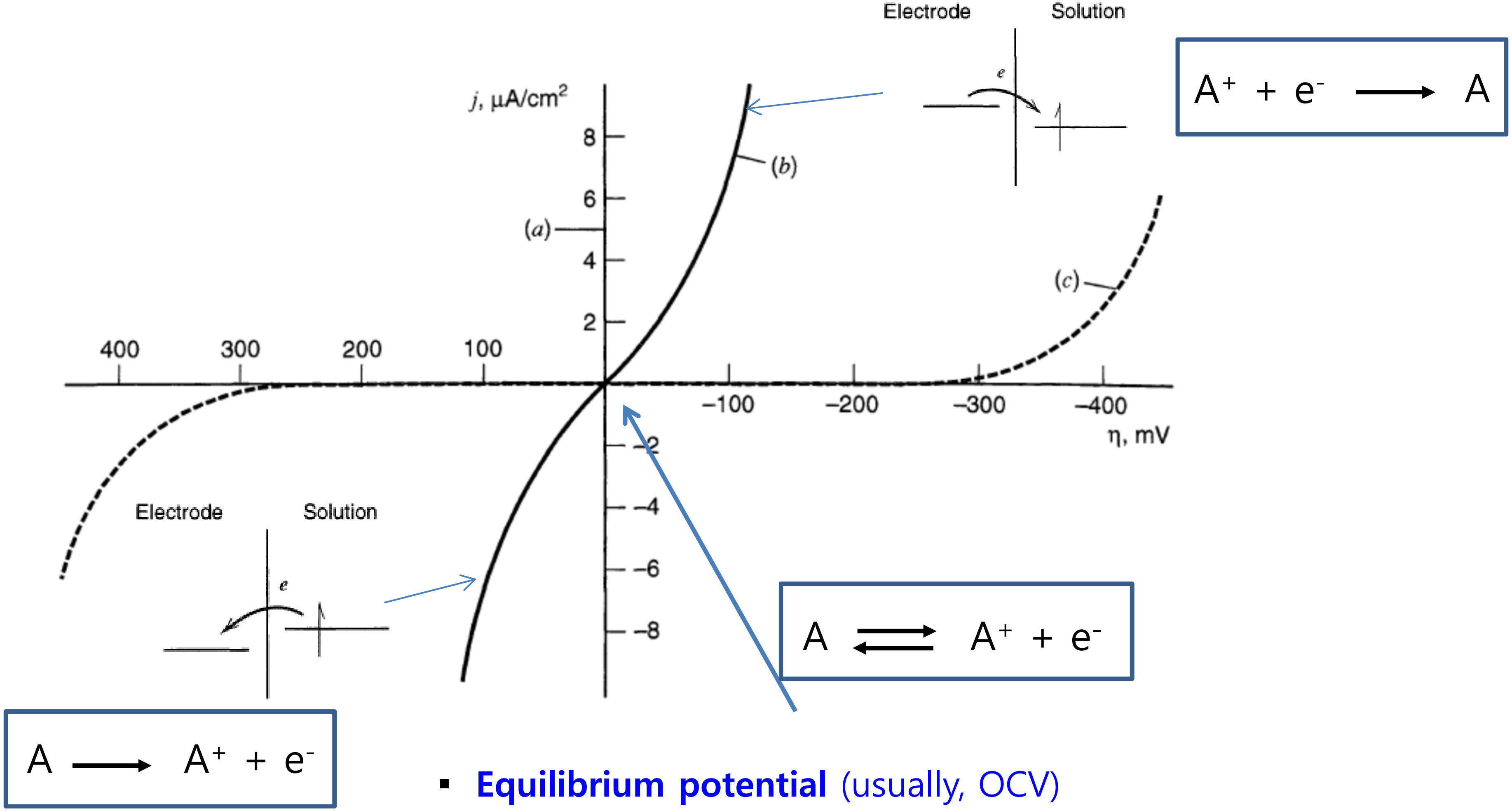


(a) Ideal polarizable electrode



(b) Ideal nonpolarizable electrode

# 1.3 Faradaic Processes



$A^+ + e^- \longrightarrow A$

$A \rightleftarrows A^+ + e^-$

$A \longrightarrow A^+ + e^-$

- **Equilibrium potential** (usually, OCV)

➔ electrode potential at the equilibrium state for redox reactions

➔ zero current at this potential

➔ depends on concentration, temperature, and pressure