EPFL

Energy Conversion by Semiconductor Devices

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Photoelectrochemistry

- **Electrochemistry: electricity + chemical reactions.**
  The oxidation–reduction reaction that occurs during an electrochemical process consists of two half-reactions, one representing the oxidation process and one the reduction process. The sum of the half-reactions gives the overall chemical reaction.

- **Photoelectrochemistry: electricity + chemical reactions + light.**
  Study within physical chemistry concerned with the interaction of light with electrochemical system (electron excitation in photoexcited material, charge transfer, electrochemical reaction)

Redox Reaction

- In redox reactions, electrons are transferred from one species to another.
- A species losing electrons is said to be oxidized; one gaining electrons is said to be reduced.
- The two processes together are called redox and one can never occur without the other.
- Both mass and charge must be balanced in any chemical reaction.

$$\boldsymbol{O(sol) + ne^{-}(m) \underset{k_{ox}}{\overset{k_{red}}{\rightleftarrows}} R(sol)}$$

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Ex) Balance the reaction: $2Mg\ (s) + O_2\ (g) \rightarrow MgO\ (s)$

$O_2 + 2e^- \rightarrow O^{2-}$ **Reduction** half-reaction

$Mg \rightarrow Mg^{2+} + 2e^-$ **Oxidation** half-reaction

Electrochemical Cells

- **Anode (oxidation):** the electrode that releases electrons to the external circuit and oxidizes during the electrochemical reaction.
- **Cathode (reduction):** the electrode that acquires electrons from the external circuit and is reduced during the electrochemical reaction.
- When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an **electrolyte**: the medium that provides the ion transport mechanism between the cathode and anode of a cell, thereby maintaining the system's electrical neutrality.
- Electrolytes are often thought of as liquids, such as water or other solvents, with dissolved salts, acids, or alkalis that are required for ionic conduction. It should however be noted that many batteries including the conventional batteries contain solid electrolytes that act as ionic conductors at RT.

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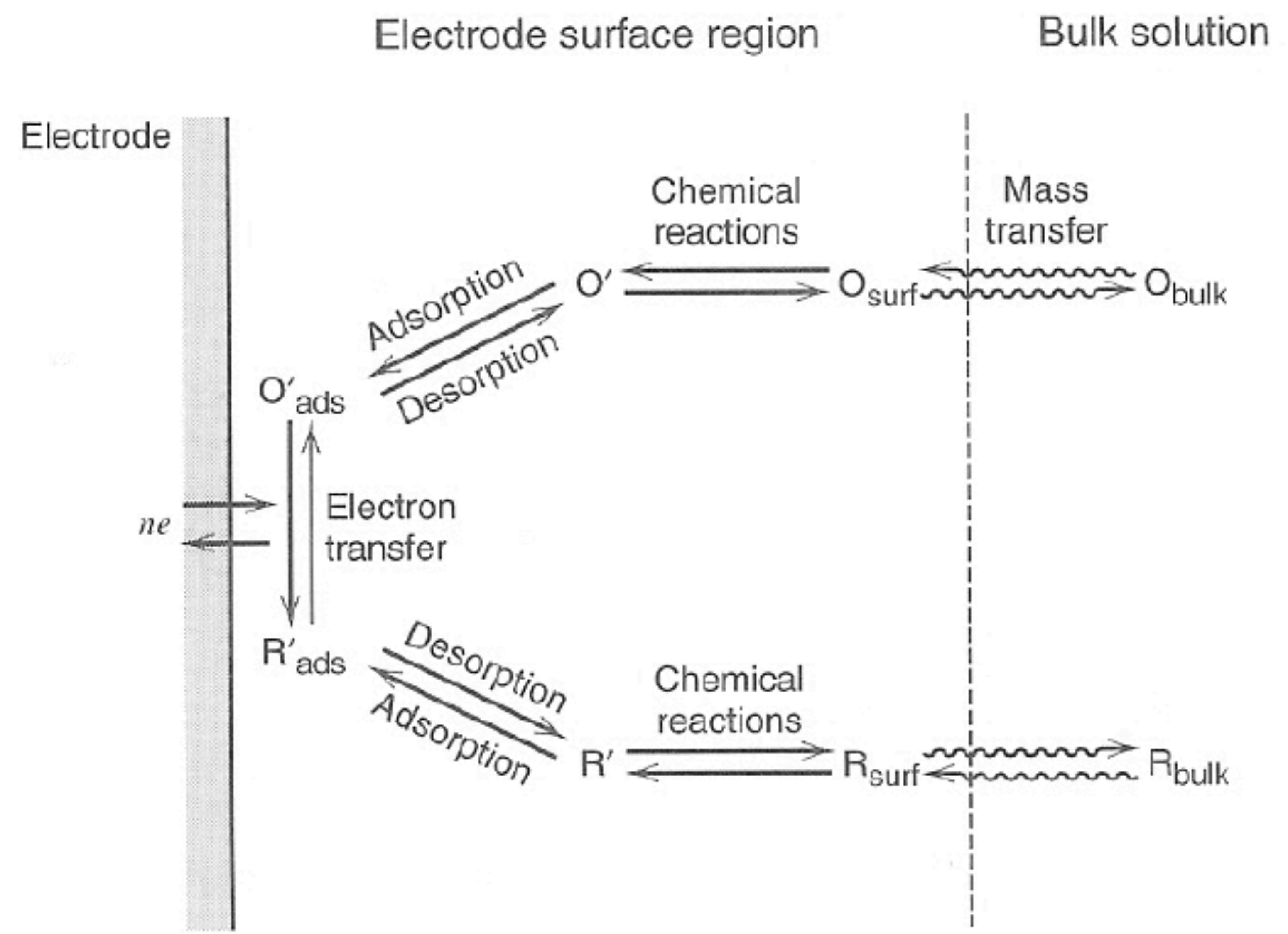
Factors Affecting Electrode Reaction Rate and Current



1. **Mass transfer**

2. **Electron transfer at the electrode surface**

3. **Chemical reactions**

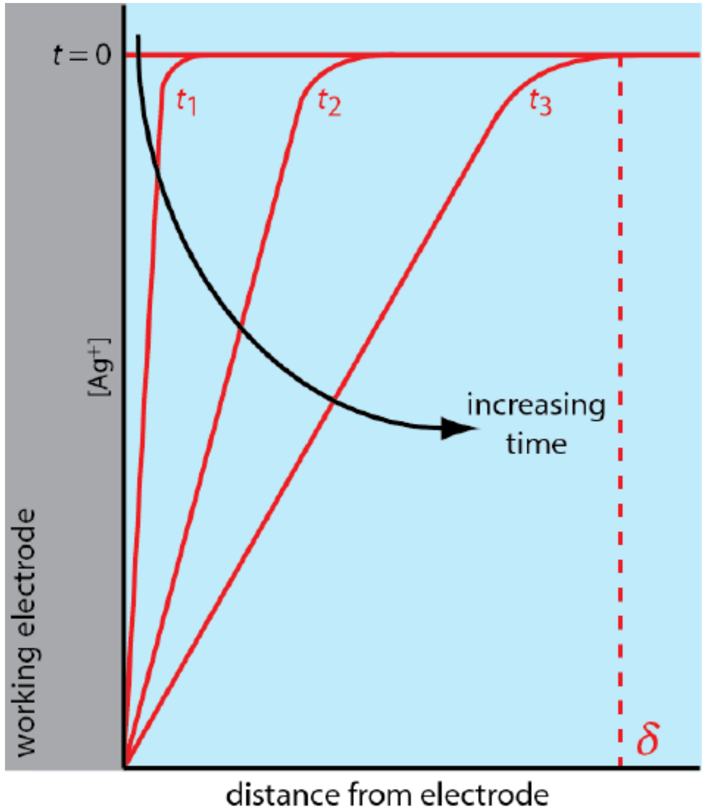
4. **Other surface reactions: adsorption, desorption, growth (electrodeposition)**

Mass Transport Modes

1. **Migration:** movement of a charged species under the influence of an electric field (a gradient of electric potential). An anion will move toward the electrode and a cation will move toward the bulk solution if the electrode is positively charged.

2. **Diffusion:** movement of species under the influence of gradient of chemical potential (a concentration gradient)

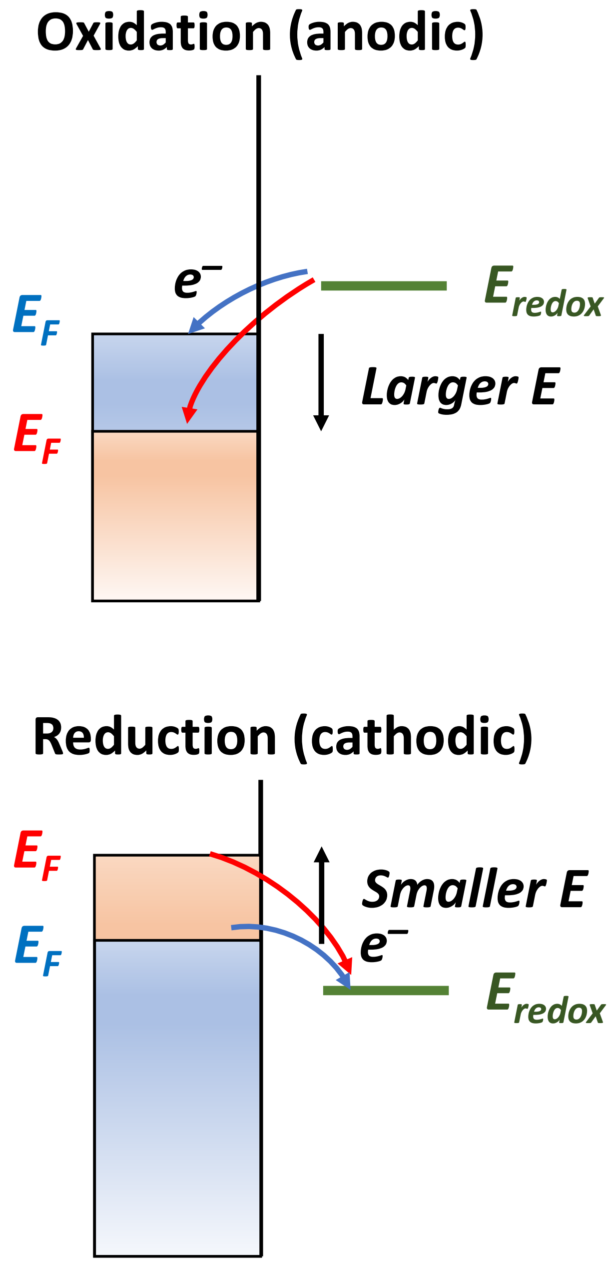
3. **Convection:** stirring or hydrodynamic transport. The most common form of convection is stirring the solution with a stir bar and other methods include rotating the electrode and incorporating the electrode into a flow-cell.



$$Ag^{+}(aq) + e^{-} \leftrightarrow Ag\ (s)$$

Electron Transfer (Faradaic Process)

- The electrode reaction (different from ordinary chemical reactions) in that at least one partial reaction must be a charge transfer reaction.
- The reaction depends on the distributions of species (concentrations and pressures), temperature, and electrode potential.
- Assumption: the electrode material itself is inert (catalyst), not undergoing any chemical transformation.
- The highest occupied electron level in the electrode = $\boldsymbol{E_F}$. Electrons are always transferred to or from this level.
- The electrode potential $\boldsymbol{E}$ of an electrode through which a current flows differs from the equilibrium potential $\boldsymbol{E_{eq}}$ established when no current flows.



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Electron Transfer (Faradaic Process)

- For simplicity, let's consider a single electron transfer reaction between two species ($\boldsymbol{O}$) and ($\boldsymbol{R}$).

$$\boldsymbol{O(sol) + e^{-}(m) \underset{k_{ox}}{\overset{k_{red}}{\rightleftarrows}} R(sol)}$$

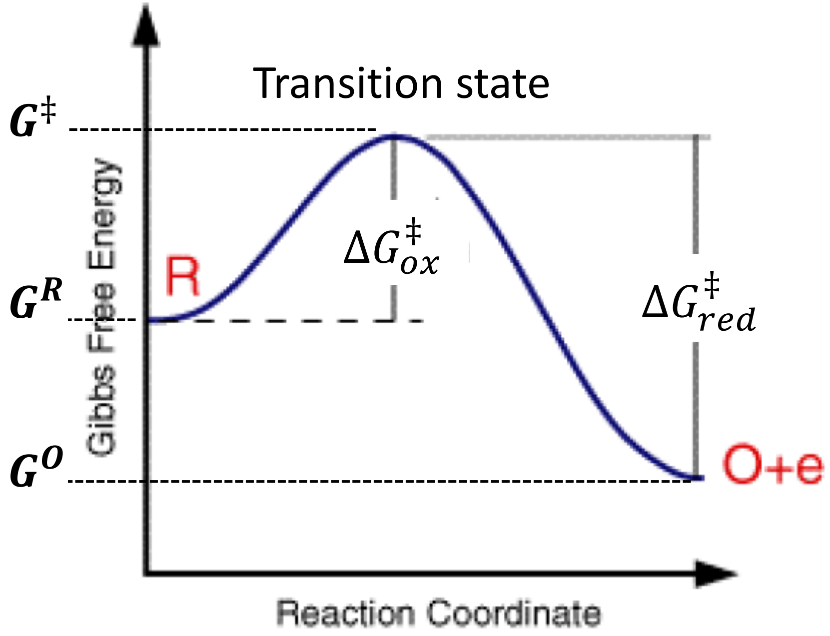
- The current flowing in either the reductive or oxidative steps can be predicted using the following expressions:

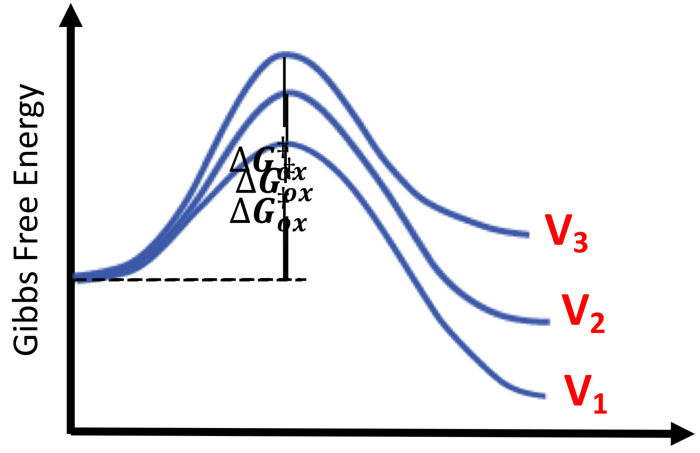
$$\boldsymbol{i_{red} = i_c = FAk_{red}[O]_0}$$

$$\boldsymbol{i_{ox} = i_a = FAk_{ox}[R]_0}$$

- The current ($\boldsymbol{i_c}$ or $\boldsymbol{i_a}$) is related to the electrode area ($\boldsymbol{A}$), the surface concentration of the reactant $\boldsymbol{[O]_0}$ or $\boldsymbol{[R]_0}$, the rate constant for the electron transfer ($\boldsymbol{k_{red}}$ or $\boldsymbol{k_{ox}}$).
  $\boldsymbol{F}$ is the Faraday constant, 96485 C/mol.

Electron Transfer (Faradaic Process)





The activation free energy for the reduction and oxidation reactions are:

$$\Delta G^{\ddagger}_{red} = G^{\ddagger} - G^{O}$$

$$\Delta G^{\ddagger}_{ox} = G^{\ddagger} - G^{R}$$

The reaction rates are:

$$k_{red} = A_{red} exp\left(\frac{-\Delta G^{\ddagger}_{red}}{RT}\right)$$

$$k_{ox} = A_{ox} exp\left(\frac{-\Delta G^{\ddagger}_{ox}}{RT}\right)$$

As a function of voltage, the plots alter:

$$\Delta G^{\ddagger}_{red} = \Delta G^{\ddagger}_{red,\, no\, V} + \alpha F V$$

$$\Delta G^{\ddagger}_{ox} = \Delta G^{\ddagger}_{ox,\, no\, V} - (1-\alpha) F V$$

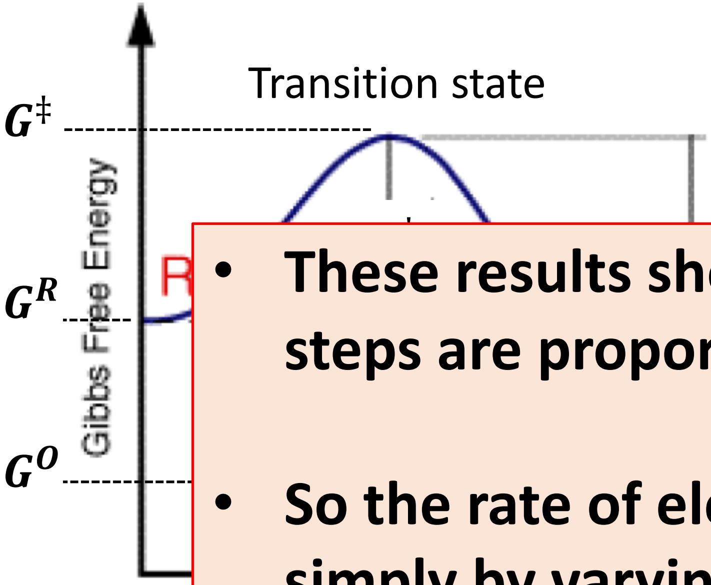
(α = transfer coefficient)

The reaction rates are:

$$k_{red} = A_{red} exp\left\{\left(\frac{-\Delta G^{\ddagger}_{red,\, no\, V}}{RT}\right)\left(\frac{-\alpha F V}{RT}\right)\right\}$$

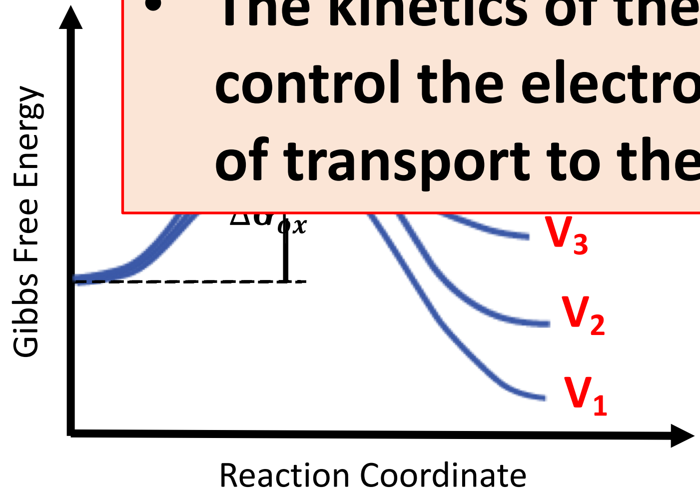
$$k_{ox} = A_{ox} exp\left\{\left(\frac{-\Delta G^{\ddagger}_{ox,\, no\, V}}{RT}\right)\left(\frac{(1-\alpha) F V}{RT}\right)\right\}$$

Electron Transfer (Faradaic Process)



The activation free energy for the reduction and oxidation reactions are: $\Delta G^{\ddagger}_{red} = G^{\ddagger} - G^{O}$

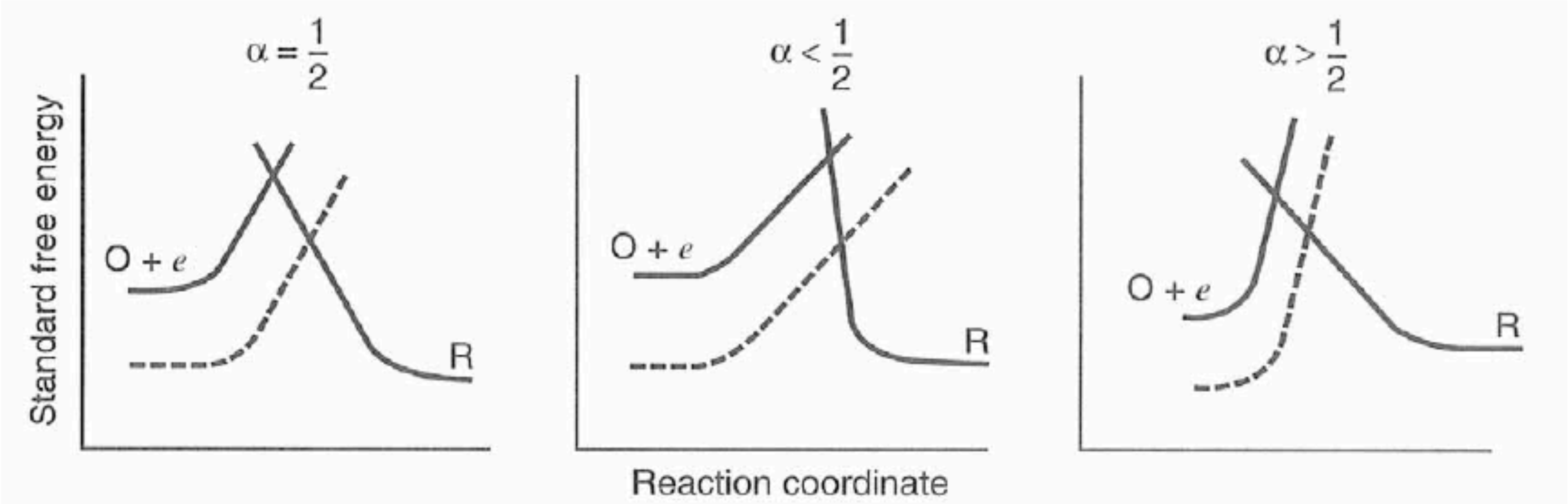
- **These results show us the that rate constants for the electron transfer steps are proportional to the exponential of the applied voltage.**
- **So the rate of electrochemical reaction e.g. electrolysis can be changed simply by varying the applied voltage.**
- **The kinetics of the electron transfer is not the only process which can control the electrochemical reaction. In many circumstances it is the rate of transport to the electrode which controls the overall reaction.**



The reaction rates are: $k_{red} = A_{red} exp\left\{\left(\frac{-\Delta G^{\ddagger}_{red,\, no\, V}}{RT}\right)\left(\frac{-\alpha FV}{RT}\right)\right\}$

$$k_{ox} = A_{ox} exp\left\{\left(\frac{-\Delta G^{\ddagger}_{ox,\, no\, V}}{RT}\right)\left(\frac{(1-\alpha)FV}{RT}\right)\right\}$$

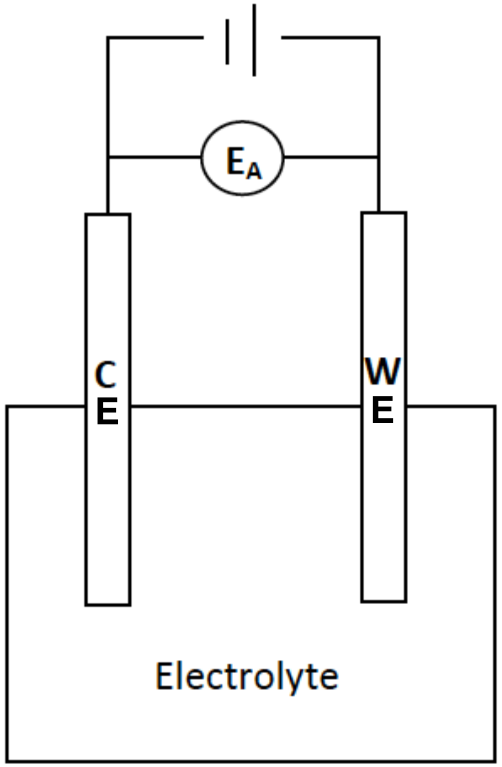
Electron Transfer (Faradaic Process)

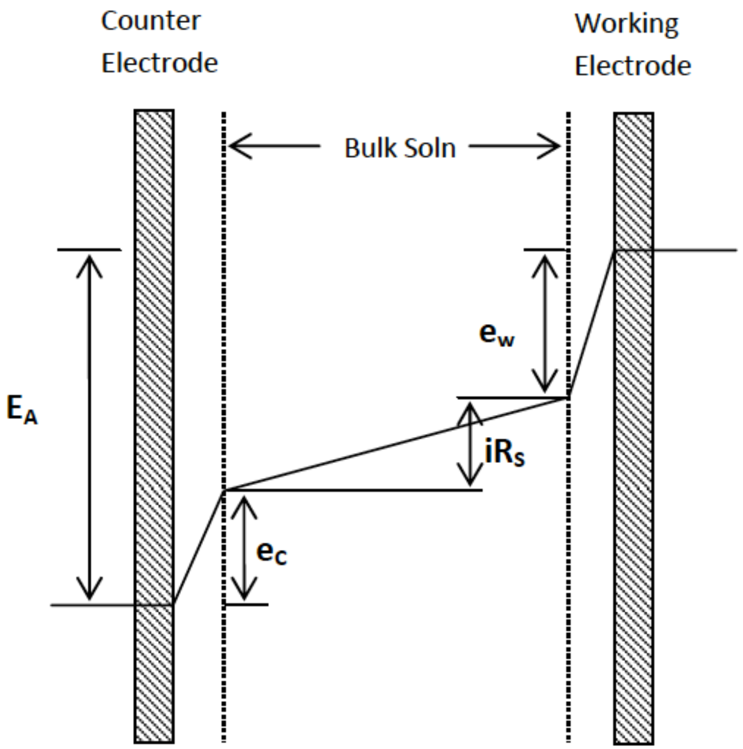


In most systems, $\mathbf{0.3} < \boldsymbol{\alpha} < \mathbf{0.7}$

Electrochemical Cells

Two electrode cell: $\mathbf{IR_s}$ problem due to high current flow





WE: Working Electrode
CE: Counter Electrode

$\mathbf{E_A}$: Applied potential

- The CE in the two electrode set-up serves two functions: It completes the circuit allowing charge to flow through the cell, and it also maintains a constant interfacial potential, regardless of current.
- In a two electrode system, it's very difficult to maintain a constant CE potential (e_C) while current is flowing.
- Along with a lack of compensation for the voltage drop across the solution (iR_S), it leads to poor control of the WE potential (e_W) with a two electrode system.

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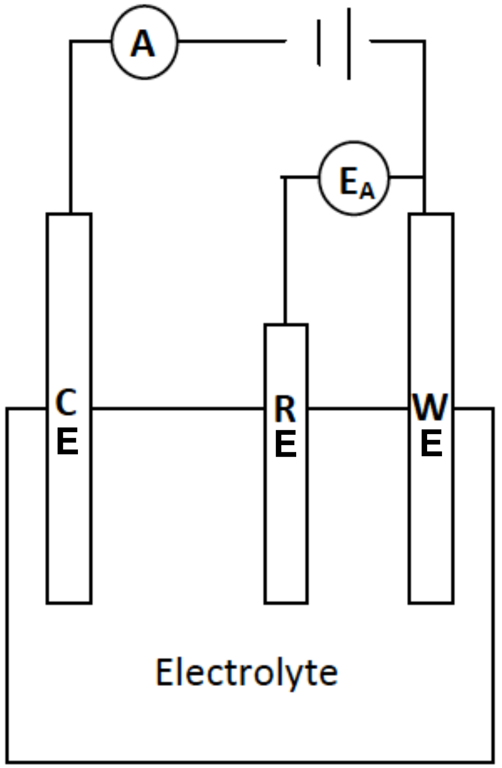
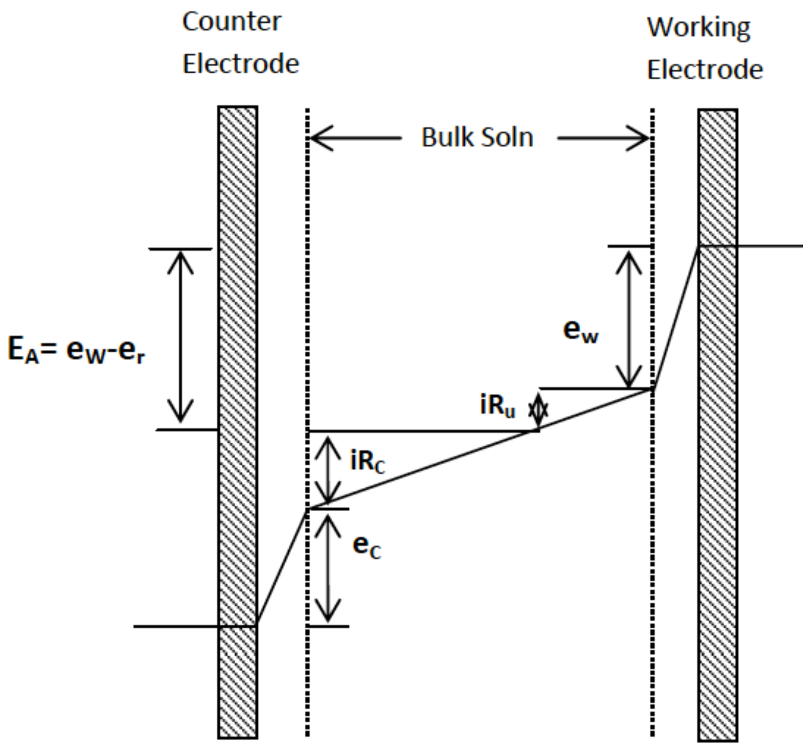
Three electrode cell: **Current between WE and CE**

Potential measurement between WE and RE

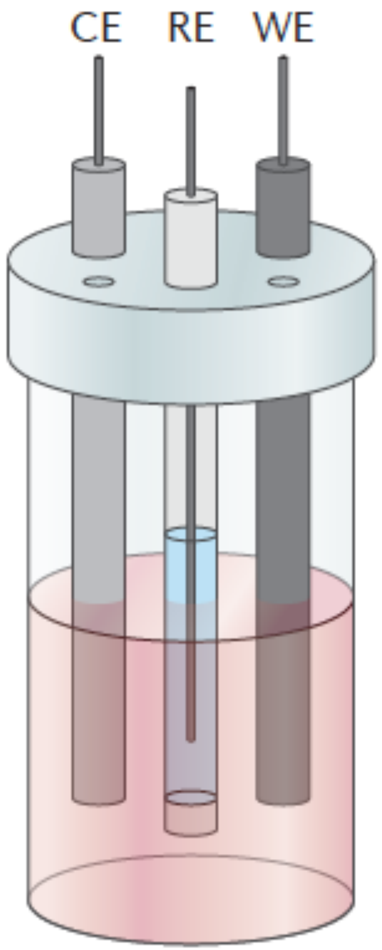


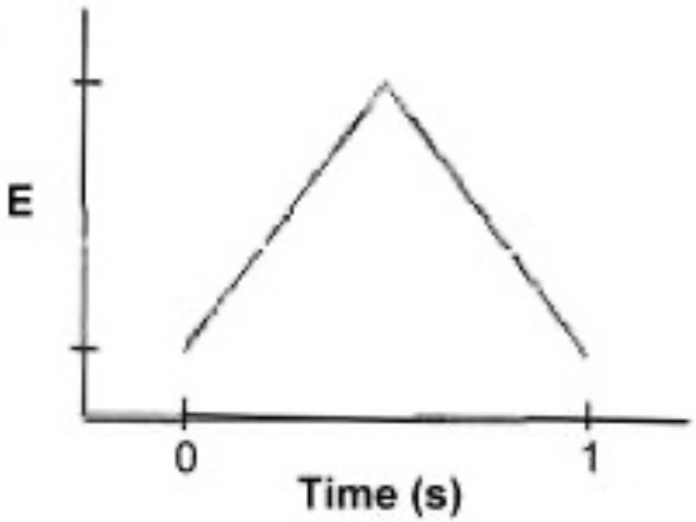


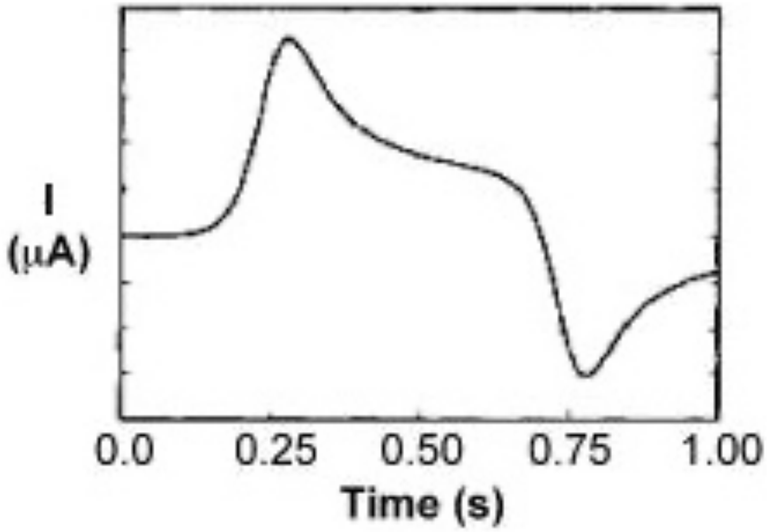
- The RE's role is to act as a reference in measuring and controlling the WE potential, without passing any current: a constant electrochemical potential at low current density.
- As the RE passes negligible current, the iR drop between the RE and WE (iR_U) is very small.
- In the three electrode configuration, the only role of the CE is to pass all the current needed to balance the current observed at the WE.

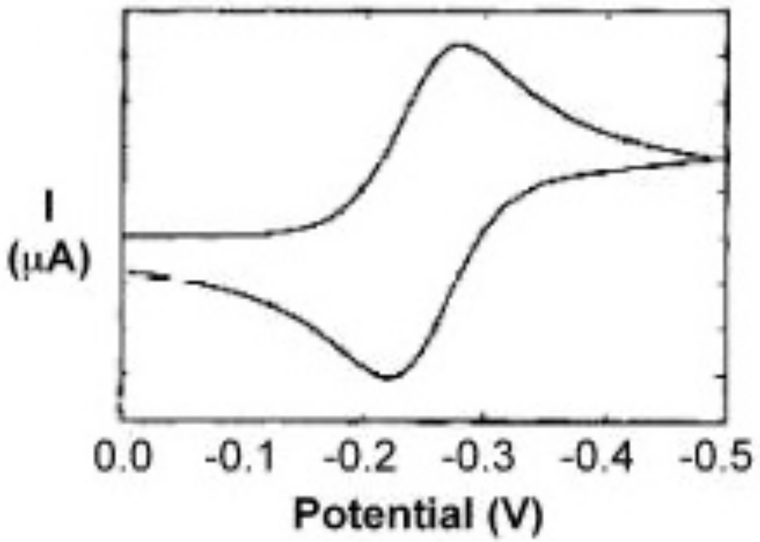
WE: Working Electrode
RE: Reference Electrode
CE: Counter Electrode

Cyclic Voltammetry









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Cyclic Voltammetry

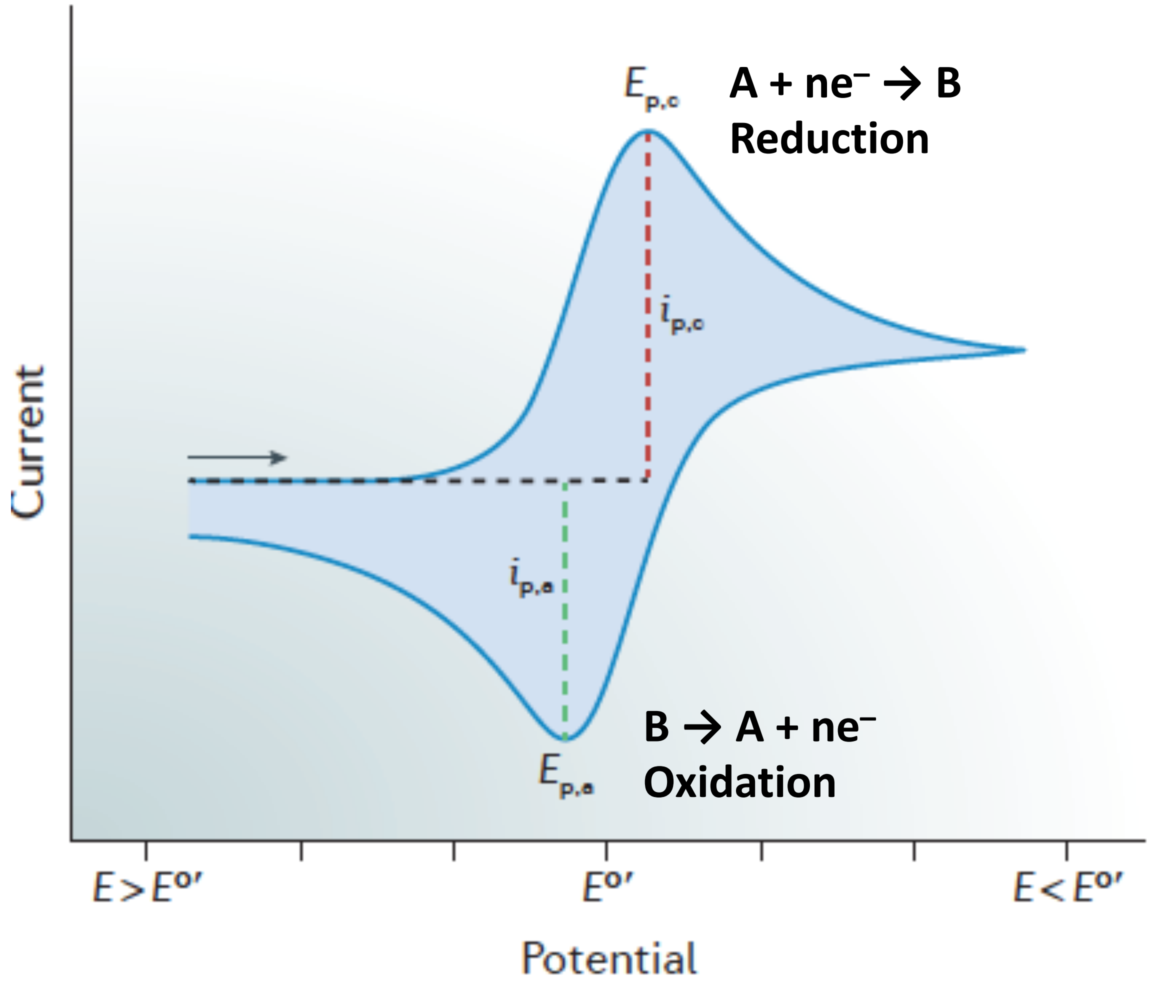


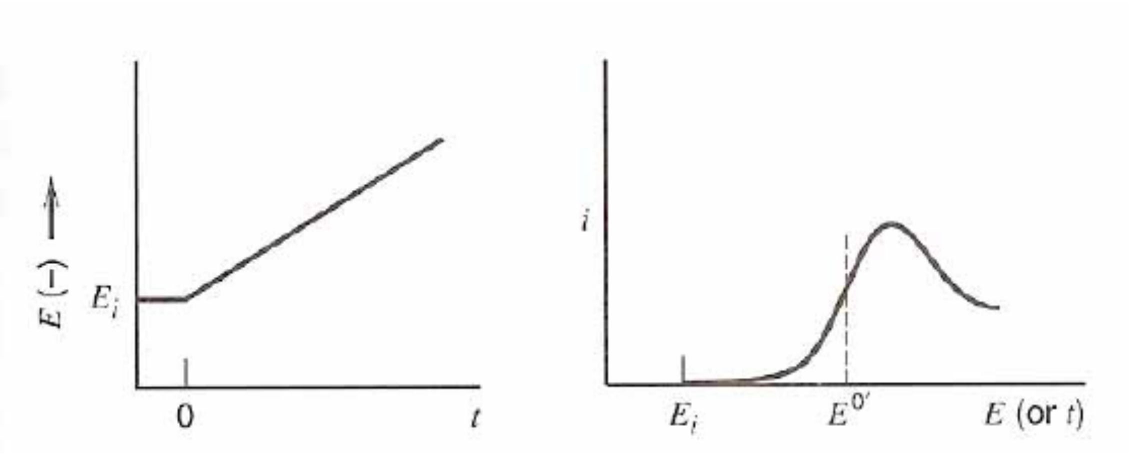
Image taken from K. J. Lee et al., *Nat. Rev. Chem.*, **1**, 0039 (2017)

- The potential is swept negative: Cathodic current flows to effect reduction reaction.
- More negative potential = greater driving force for reduction.
- But the concentration of A is depleted near the electrode surface due to the limited diffusion rate of A to the electrode surface → A is depleted and B is accumulated.
- After the direction of the potential is reversed, a second current peak appears, corresponding to oxidation reaction.

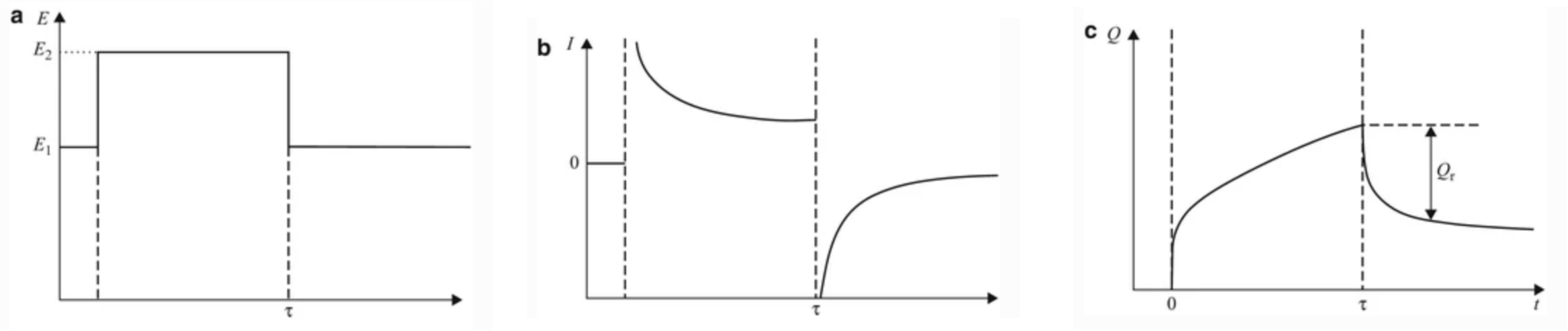
$i_{p,c}$: The cathodic peak current
$E_{p,c}$: The cathodic peak potential
$i_{p,a}$: The anodic peak current
$E_{p,c}$: The anodic peak potential

The Other Measurement Modes

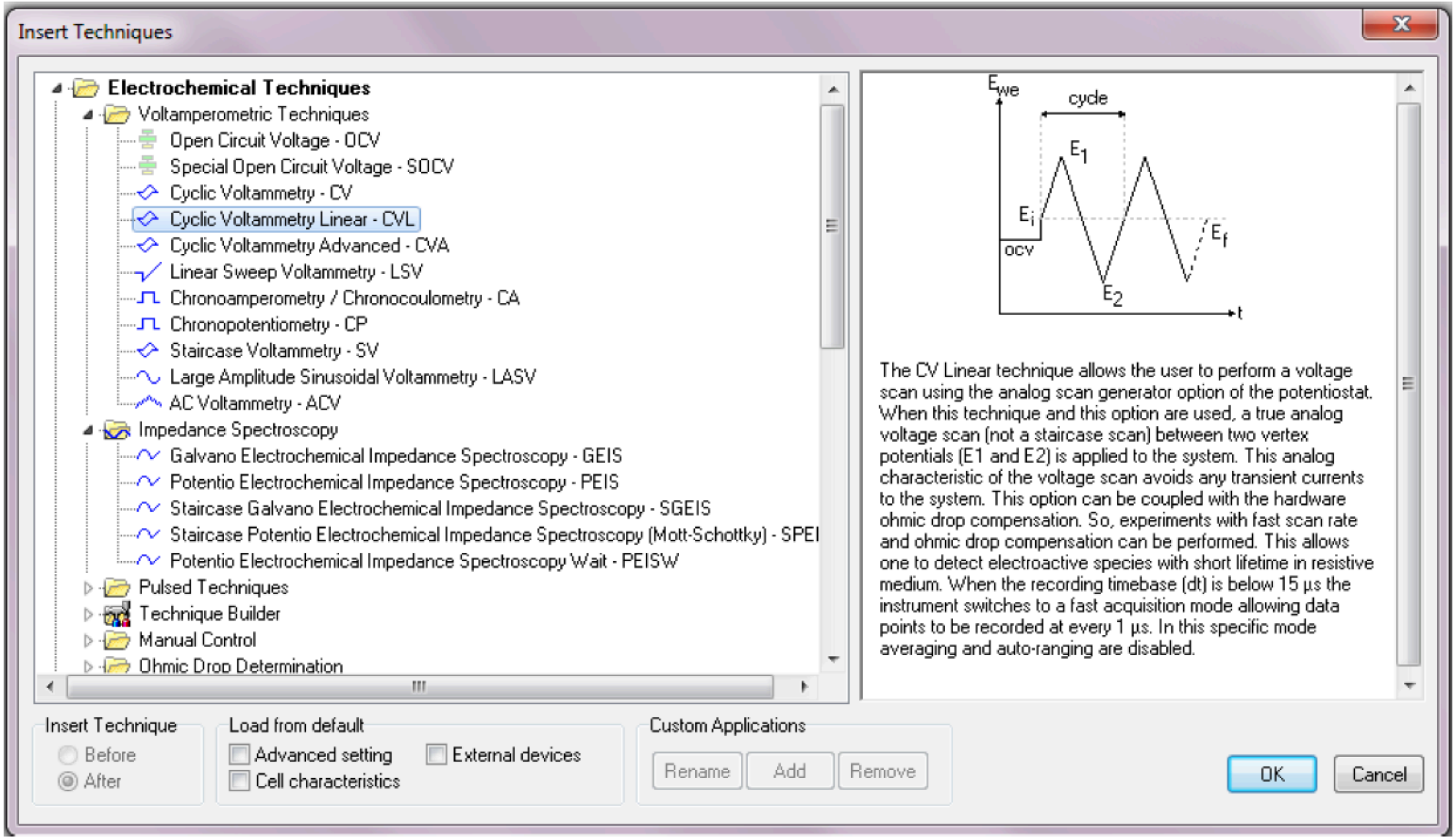
Linear Sweep Voltammetry (LSV)



Chronoamperometry / Chronocoulometry (CA)



The Other Measurement Modes



Cell Potential & Gibbs Energy

- The total amount of energy produced by an electrochemical cell (the amount of energy available to do electrical work) depends on both **the cell potential** and **the total number of electrons** that are transferred from the reductant to the oxidant during the course of a reaction.

- The maximum amount of work that can be produced by an electrochemical cell (W_{max}) = product of the cell potential (E_{cell}) and the total charge transferred during the reaction (nF)

$$\boldsymbol{W_{max}\ or\ \Delta G}\ \text{(J)} = -E_{cell}\ \text{(V or J/C) x charge (C)}$$
$$= -E_{cell}\ \text{x number of electrons x electric charge per electron}$$
$$= -E_{cell}\ \text{x moles of electrons x electric charge per mole}$$
$$= -E_{cell} \times n \times F$$

F (Faraday constant) = the charge on 1 mol of electrons = (6.02214×10^{23} J/mol) x (1.60218×10^{-19} C)
= 96,485 C/mol (J/(V·mol)

$$\boldsymbol{W_{max}\ or\ \Delta G = -nFE_{cell}}$$

If the reaction is spontaneous, $\boldsymbol{\Delta G < 0}$

$\boldsymbol{E_{cell} > 0}$

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Standard Electrode Potential

- When both reactants and products are in their standard states, $\Delta G^{\circ} = -nFE^{\circ}_{cell}$
- The standard cell potential (V) is the potential difference between the cathode and anode: $E^{\circ}_{cell} = E^{\circ}_{cathode\ (red)} - E^{\circ}_{anode\ (red)}$
- The cell potential is called the cell electromotive force (emf) of the cell when no current is drawn through the cell.
- Standard Reduction Potential: **$A^{z+} + ze^{-} \rightarrow A$**
- Standard oxidation potential = −(standard reduction potential): **$A \rightarrow A^{z+} + ze^{-}$**
- The standard cell potential (V): $E^{\circ}_{cell} = E^{\circ}_{cathode\ (red)} + E^{\circ}_{anode\ (ox)}$

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Standard Electrode Potential

Reduction potential measures the tendency of a chemical species to acquire electrons and thereby be reduced.

The standard reduction potential (E^0) is measured under standard conditions:

- 25 °C (298 K)
- 1 M concentration for each ion participating in the reaction
- Partial pressure of 1 atm for each gas that is part of the reaction
- Metals in their pure states

Universally, hydrogen has been recognized as having reduction and oxidation potentials of zero.

Standard Reduction Potential

Reaction	E^0 (V) (SHE)	Reaction	E^0 (V) (SHE)
$Li^+ + e^- \rightleftharpoons Li$	−3.045	$HgO + H_2O + 2e^- \rightleftharpoons Hg + 2OH^-$	0.098
$K^+ + e^- \rightleftharpoons K$	−2.935	$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	0.154
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	−2.866	$Cu^{2+} + e^- \rightleftharpoons Cu^+$	0.153
$Na^+ + e^- \rightleftharpoons Na$	−2.714	$AgCl + e^- \rightleftharpoons Ag + Cl^-$	0.2224
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.363	$HgCl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-$	0.2676
$Al^{3+} + 3e^- \rightleftharpoons Al$	−1.662	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	0.337
$Ti^{2+} + e^- \rightleftharpoons 2e^- \rightleftharpoons Ti$	−1.628	$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$	0.36
$Zn(OH)_2 + 2e^- \rightleftharpoons Zn + 2OH^-$	−1.245	$Cu^{2-} + e^- \rightleftharpoons Cu$	0.521
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	−1.180	$I_2 + 2e^- \rightleftharpoons 2I^-$	0.536
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^{2-}$	−0.822	$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0.682
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.764	$Fe^{3+} + e^- \rightleftharpoons e^- \rightleftharpoons Fe^{2+}$	0.771
$S + 2e^- \rightleftharpoons S^{2-}$	−0.48	$Br_2 + 2e^- \rightleftharpoons 2Br^-$	1.065
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.441	$\boxed{O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O}$	$\boxed{1.229}$
$Cd^{2+} + 2e^- \rightleftharpoons Cd$	−0.403	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	1.358
$Ni^{2-} + 2e^- \rightleftharpoons Ni$	−0.250	$PbO_2 + 4H^+ + e^- \rightleftharpoons Pb^{2+} + 2H_2O$	1.455
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0.136	$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	1.61
$\boxed{2H^+ + 2e^- \rightleftharpoons H_2}$	$\boxed{0.0000}$	$F_2 + 2e^- \rightleftharpoons 2F^-$	1.87

Standard Electrode Potential

Ex) Standard cell potential in the galvanic cell reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Half-cell reactions:
Cathode (reduction): $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$
Anode (oxidation): $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$

The cell can be represented as:
$Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$

$$E^{\circ}_{Cu2+/Cu} = 0.337\ V$$

$$E^{\circ}_{Zn2+/Zn} = -0.764\ V$$

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = E^{\circ}_{Cu2+/Cu} - E^{\circ}_{Zn2+/Zn} = 0.337\ V - (-0.764\ V) = 1.101\ V$$

Nernst Equation

The Nernst equation allows us to calculate the reduction potential of a redox reaction under "non-standard" conditions, at any temperature and concentration of reactants and products.

$$E = E^0 - \left(\frac{RT}{nF}\right) lnQ = E^0 - \frac{0.0592}{n} logQ \ (at\ 298\ K)$$

- E is the reduction potential for the specified non-standard state (not 1 M).
- E^0 is the standard reduction potential.
- R and F are the gas and Faraday constants, respectively.
- n is the number of electrons transferred in the reaction.
- Q is the reaction quotient. The brackets are concentrations and the lowercase letters are stoichiometric coefficients for the each species: $aA + bB \rightarrow cC + dD$

A and B are the reactants
C and D are the products
The lowercase letters: stoichiometric coefficients

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

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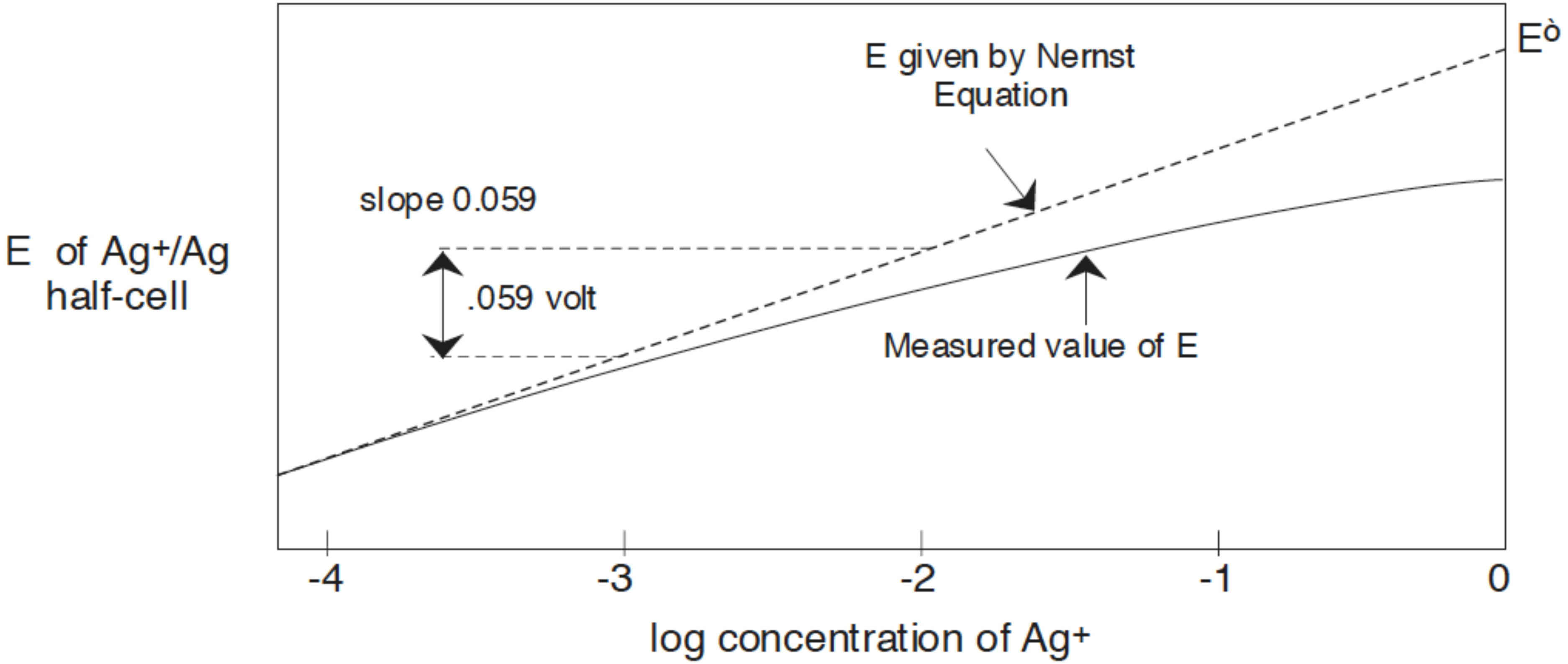
Nernst Equation

$$E = E^0 - \left(\frac{RT}{nF}\right) lnQ = E^0 - \frac{0.0592}{n} logQ \ (at\ 298\ K)$$



$a_{Red} = \gamma_{Red}[Red] = [Red]$ (at low concentration)
$a_{Ox} = \gamma_{Ox}[Ox] = [Ox]$ (at low concentration)

$a: chemial\ activity, \gamma = activity\ coefficient$

Nernst Equation

Ex) What is the cell potential of the following reaction at 298 K?

$2Al(s) + 3Cu^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Cu(s)$

$$[Al^{3+}] = 0.1M \ and \ [Cu^{2+}] = 3M$$

$Cu^{2+} + 2e^{-} \rightarrow Cu$, $E^0 = 0.337$ V and $Al^{3+} + 3e^{-} \rightarrow Al$, $E^0 = -1.662$ V

$$E^0 = 1.999\,V, Q = \frac{[Al^{3+}]^2}{[Cu^{2+}]^3} = \frac{0.1^2}{3^3} = 3.7 \times 10^{-4}, n = 6$$

$$E = 1.999 - \frac{0.0592}{6}\log(3.7 \times 10^{-4}) = 2.033\,V$$

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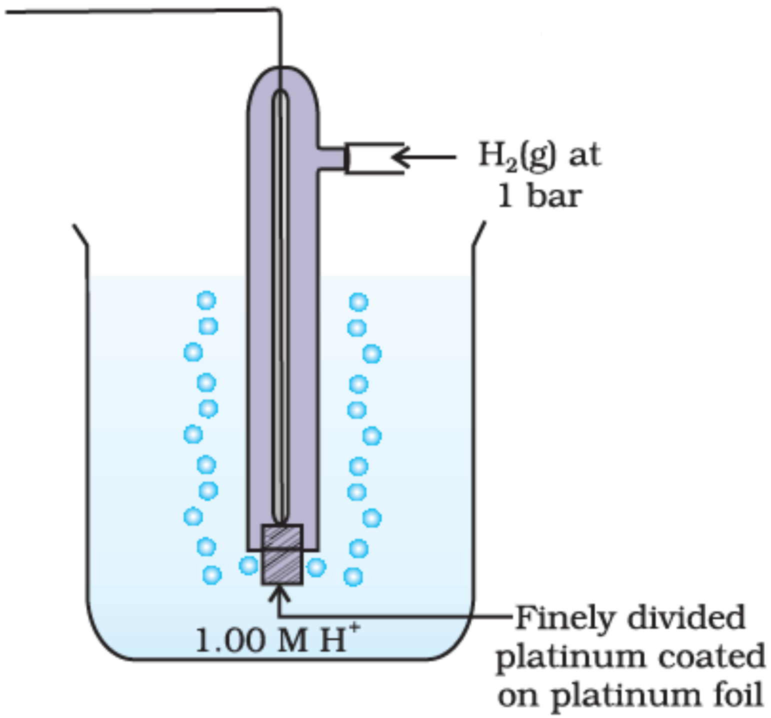
The potential of individual half-cell cannot be measured.



$$2H^+ (aq) + 2e^- \rightarrow H_2(g) \; (1 \text{ atm})$$

E^0 = 0.00 V *by definition*

- One half-reaction, the reduction of 1 M hydrogen ion on a (catalytic) platinum electrode to hydrogen gas at 1 atm is arbitrarily assigned a standard reduction potential of zero volts: Standard Hydrogen Electrode (SHE).
- All other half-cell potentials are calculated relative to the hydrogen half-cell voltage.

Standard Electrode Potential

NHE (Normal Hydrogen Electrode): potential of a platinum electrode in 1 N acid solution. NHE is constructed by immersing a platinum electrode into a solution of 1 N (normal concentration, for protons, 1 N = 1 M) protons (strong acid) and bubbling pure hydrogen gas through the solution at 1 atm pressure.

SHE (Standard Hydrogen Electrode): potential of a platinum electrode in a theoretical ideal solution (the current standard for zero potential for all temperatures). SHE is composed of a platinum electrode dipped in an ideal acidic solution containing 1 M (effective concentration) protons and bubbling pure hydrogen gas at 1 bar. The absolute potential of SHE is 4.44±0.02 V at 25 °C but its potential is set to be zero.

RHE (Reversible Hydrogen Electrode): a practical hydrogen electrode whose potential depends on the pH of the solution.

$$E_{RHE} = -0.0592pH$$

Standard Electrode Potential

$$E_{RHE} = -0.0592pH$$

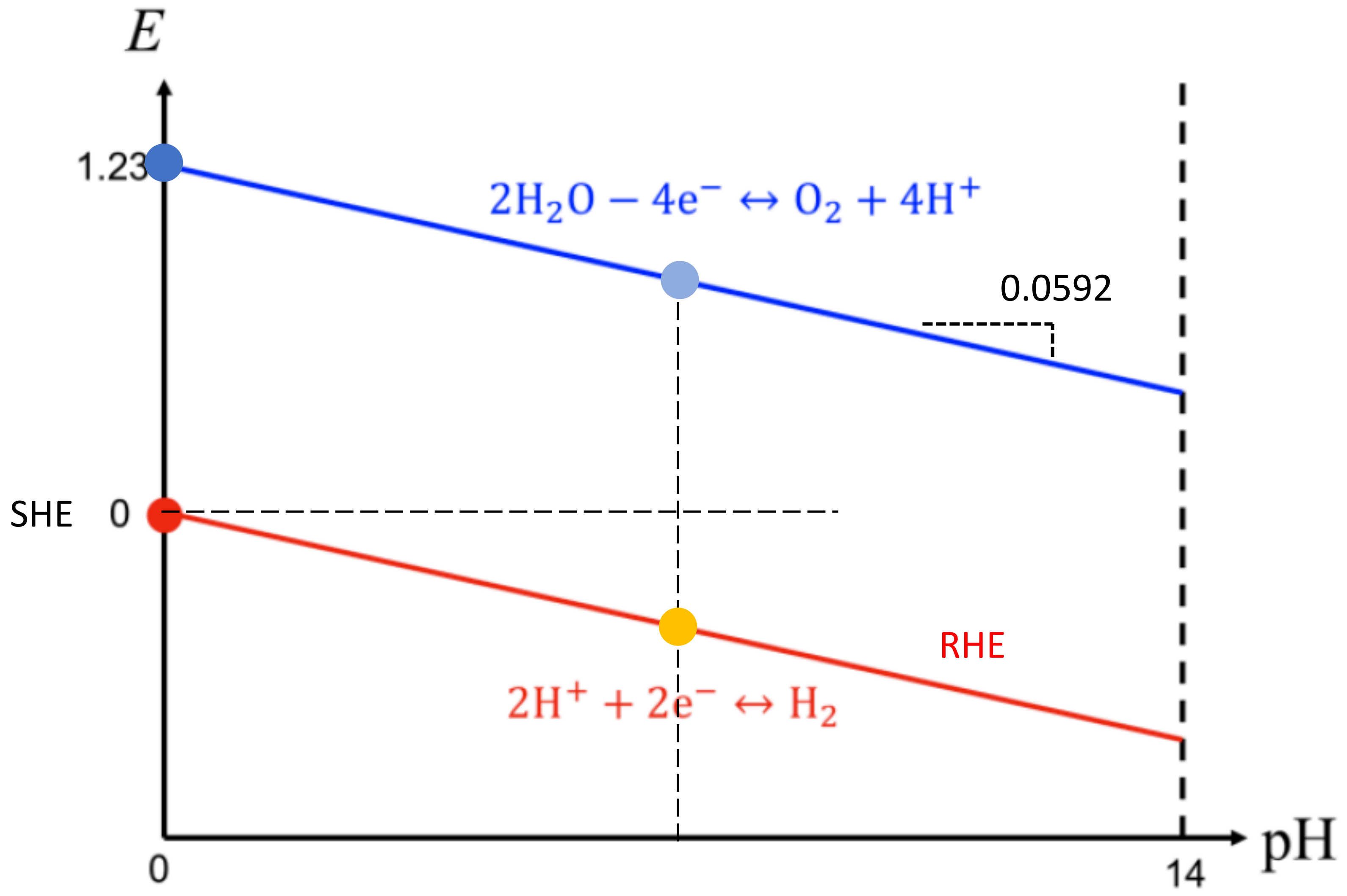
$2H^+ (aq) + 2e^- \rightarrow H_2(g)$

$$E_{H^+/H_2} = E^0_{H^+/H_2} - \frac{RT}{nF}\ln\left(\frac{p_{H_2}}{[H^+]^2}\right)$$

at 25°C and unit H_2 partial pressure

$$E_{H^+/H_2} = E^0_{H^+/H_2} - \frac{0.0592}{2} \times 2pH = -0.0592pH$$

Standard Electrode Potential



Reference Electrodes

- In most electrochemical experiments, our interested is concentrated on only one of the electrode reactions.

- Since all measurements must be on a complete cell involving two electrode systems, it is common practice to employ a reference electrode as the other half of the cell.

- The major requirements of a reference electrode is that it be **easy to prepare** and **maintain**, and that its potential be **stable**.

- The last requirement essentially means that the concentration of any ionic species involved in the electrode reaction must be held at a fixed value.

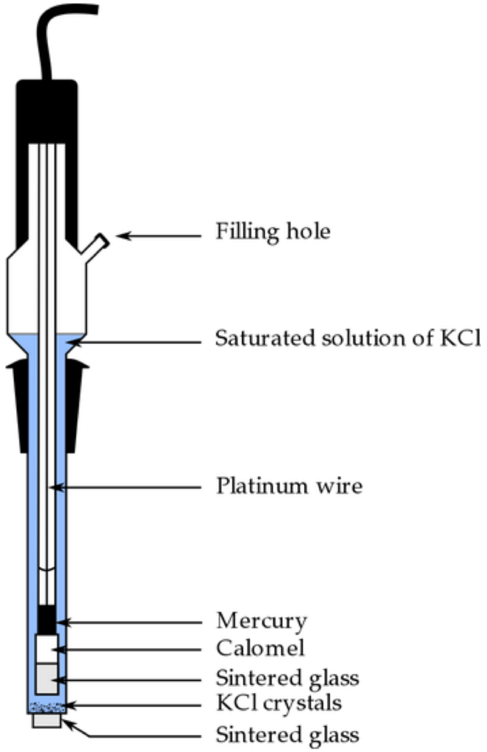
Saturated Calomel Reference Electrodes

Saturated Calomel Electrode (SCE): A reference electrode based on the reaction between elemental mercury and mercury(I) chloride (calomel). Mercury provides a stable and conductive medium for the electrode to operate. Calomel paste serves as a salt bridge that allows ion exchange while maintaining a constant chloride ion concentration. Saturated KCl solution ensures that the chloride ion concentration remains constant and prevents deviations in potential over time. A platinum wire immersed in the mercury layer allows contact with an external circuit such as a potentiometer.

$2Hg(l) + 2Cl^- = Hg_2Cl_2 + 2e^-$ $\qquad$ $Hg|Hg_2Cl_2|KCl(aq)||$

$$E_{SCE} = E^0_{Hg_2Cl_2/Hg} - 0.0592\log(a_{Cl^-})^2$$
$$= 0.268\,V - 0.0592\log(a_{Cl^-})^2$$

@ a 1.00 M of KCl, the potential is +0.280 V *vs* SHE at RT
@ a saturated solution of KCl, the potential is +0.241 V *vs* SHE at RT

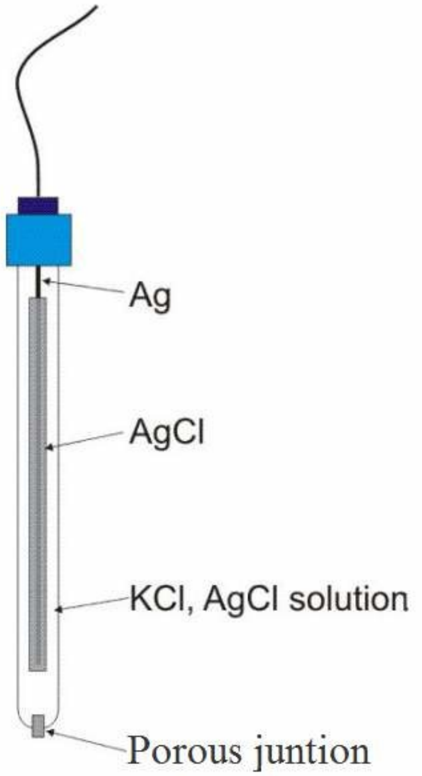


Ag/AgCl Reference Electrodes

Silver-silver chloride electrode: the silver/silver chloride electrode, which is based on the reduction of AgCl to Ag. This electrode usually consists of a silver wire, coated with a thin of AgCl. The silver-silver chloride reference electrode develops a potential proportional to the chloride concentration, whether it is sodium chloride, potassium chloride, ammonium chloride or some other chloride salt and remains constant as long as the chloride concentration remains constant. A porous plug serves as the salt bridge.

$Ag + Cl^- = AgCl(s) + e^-$ $\quad\quad$ $Ag|AgCl(s)|Cl^-(aq)||$

$$E_{AgCl/Ag} = E^0_{AgCl/Ag} - 0.0592 \log a_{Cl^-}$$
$$= 0.222\,V - 0.0592 \log a_{Cl^-}$$



@ a solution of 3.5 M KCl, the potential is +0.205 V *vs* SHE at RT
@ a saturated solution of KCl, the potential is +0.197 V *vs* SHE at RT

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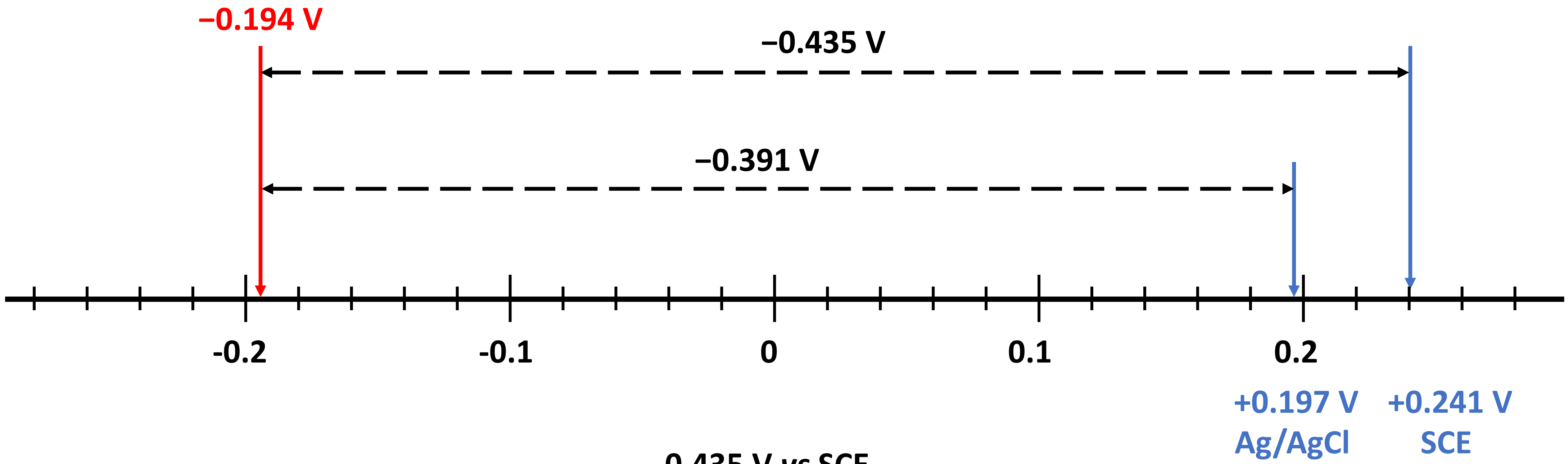
Reference Electrodes vs SHE

Ex) If an electrode has a potential of −0.435 V with respect to a SCE (sat), what is the potential with respect to a silver-silver chloride electrode (saturated KCl)? What would be the potential with respect to the SHE?

SCE: a saturated solution of KCl, the potential is +0.241 V *vs* SHE at RT

Ag/AgCl: a saturated solution of KCl, the potential is +0.197 V *vs* SHE at RT

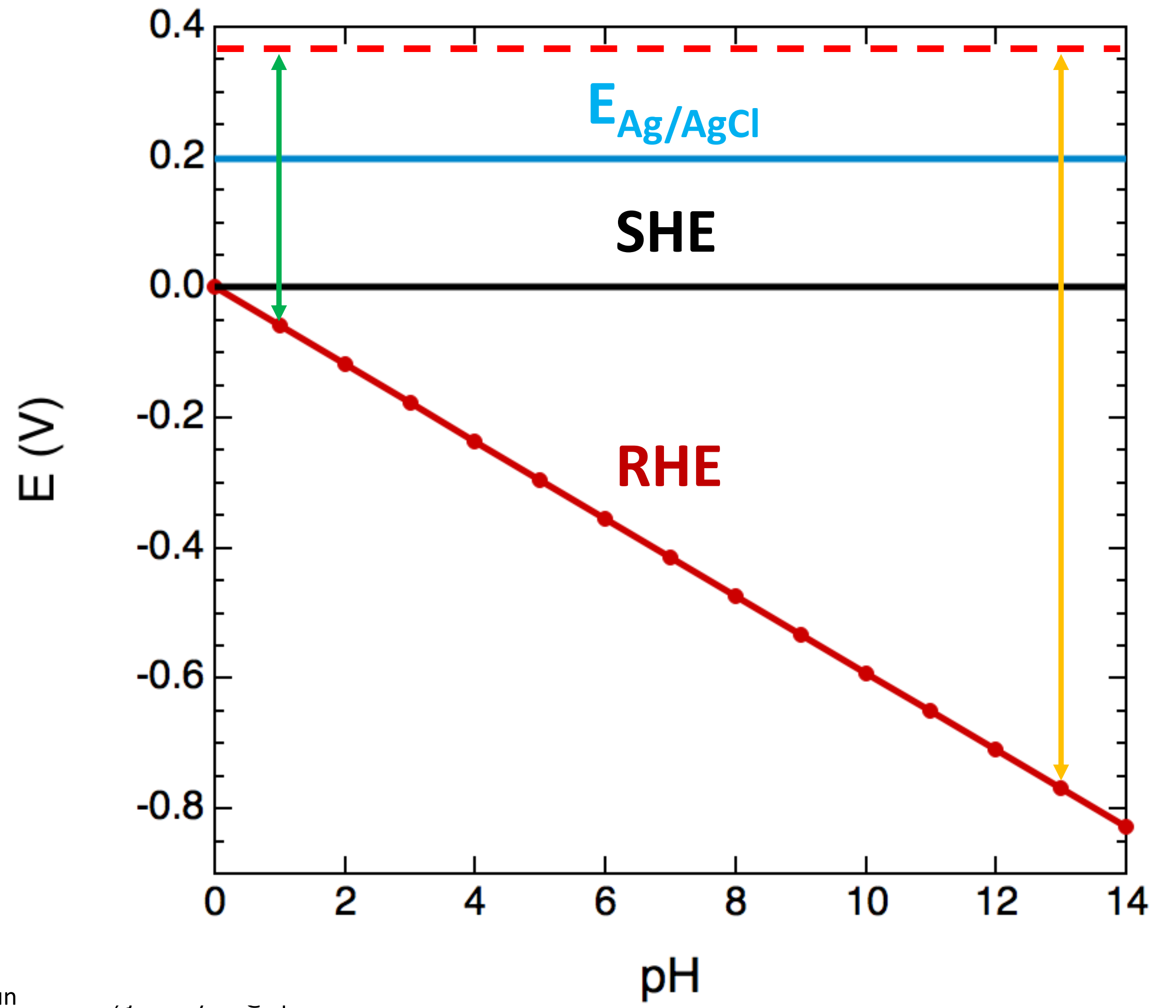


−0.435 V *vs* SCE
−0.391 V *vs* Ag/AgCl
−0.194 V *vs* SHE

Potential Relation between SHE vs RHE vs Ag/AgCl RE

E vs SHE = Recorded E + $E_{Ag/AgCl}$ (sat)

E vs RHE = Recorded E + $E_{Ag/AgCl}$ (sat) + 0.0592 pH



Ex) If an electrode has a potential of 0.153 V with respect to a Ag/AgCl RE at pH 1, what is the potential with respect to a RHE? What would be the potential with respect to the RHE at pH 13?

At pH = 1, E vs RHE = 0.153 + 0.197 + 0.0592 x 1 = **0.409 V**

At pH = 13, E vs RHE = 0.153 + 0.197 + 0.0592 x 13 = **1.120 V**

0.350 V *vs* SHE (pH independent)