Chapter 1

Introduction and Overview of Electrode Process

➔ the terms and concepts for describing electrode reactions before studying detailed electrochemical reactions with complex mathematical governing equations

1.1.1 Electrochemical Cells and Reactions

Electrochemistry

- The branch of chemistry

  → concerned with the interrelation of electrical and chemical effects.

- Deals with the study of

  → chemical changes caused by the passage of an electric current

  → the production of electrical energy by chemical reactions.

- electrophoresis, corrosion, electrochromic displays, electro analytical sensors, batteries, fuel cells, and electroplating

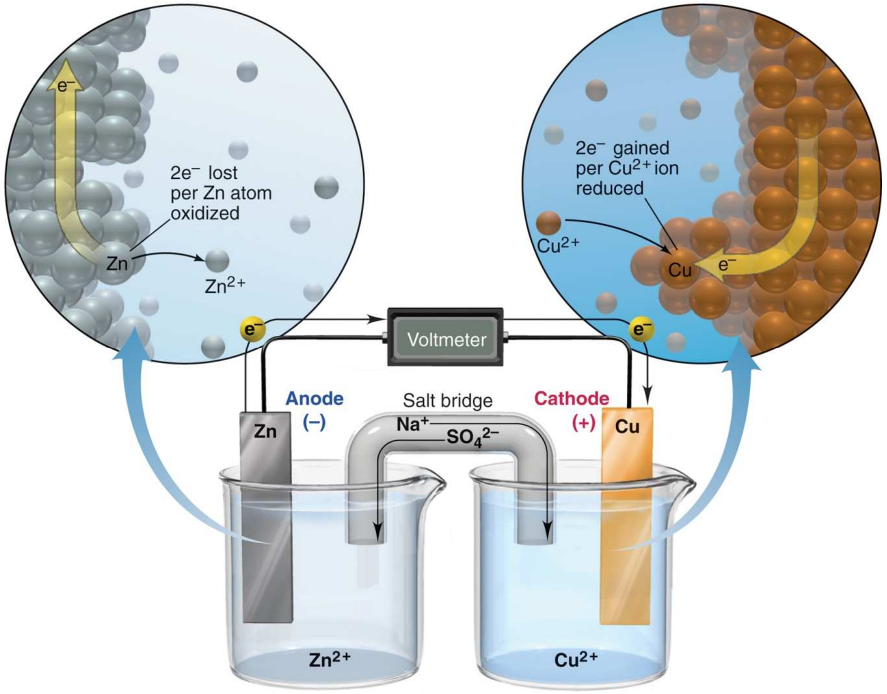
1.1.1 Electrochemical Cells and Reactions

Electrochemical system

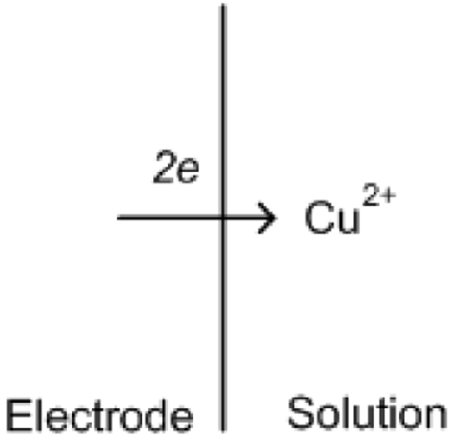
- Concerned with the processes and factors that affect the transport of charge across the interface between chemical phases

→ for example, between an electronic conductor (an electrode) and an ionic conductor (an electrolyte).

→ Typically, consists of two electrodes separated by an electrolyte



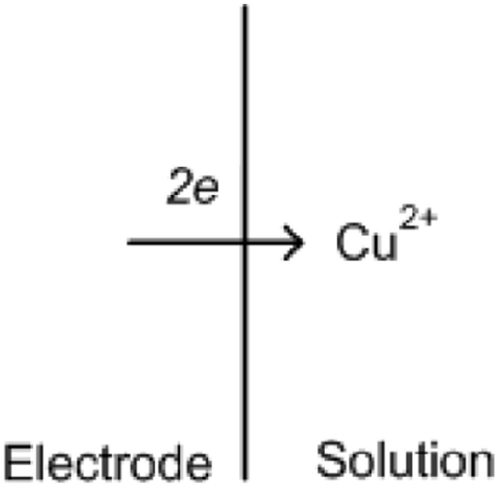
Heterogeneous charge transfer reaction

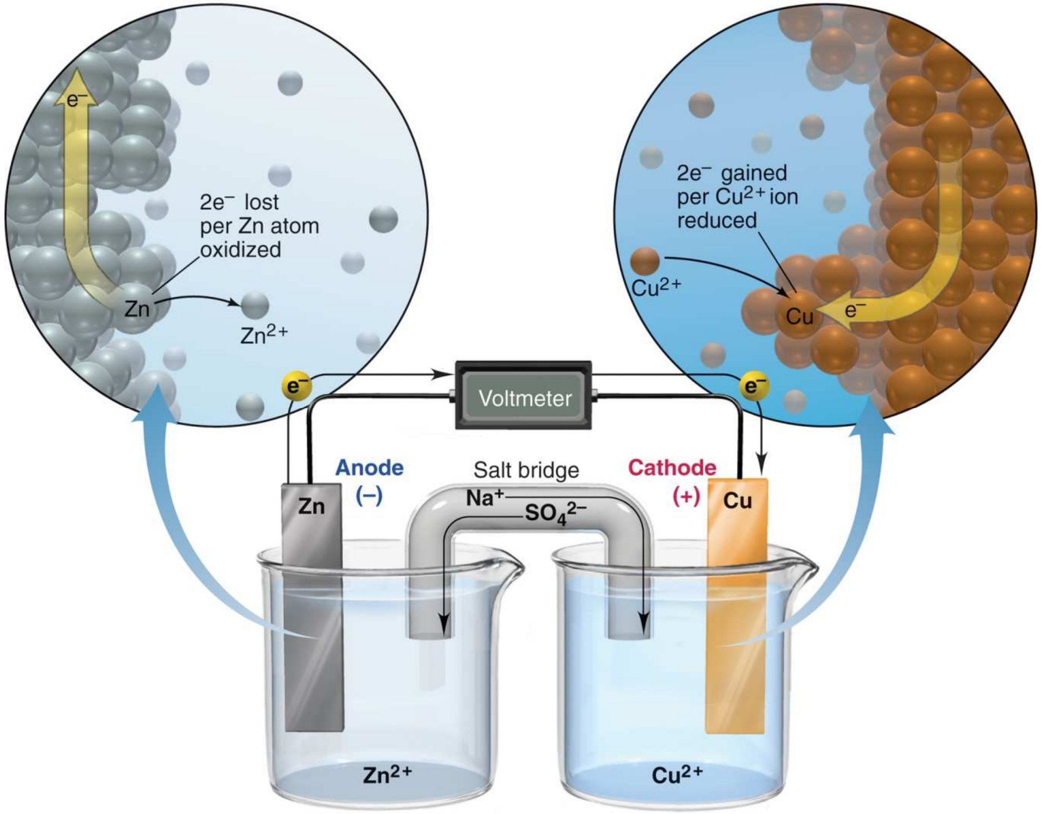


1.1.1 Electrochemical Cells and Reactions

→ In particular, concerned with the electrode/electrolyte interface and the events that occur there when an electric potential is applied and current passes.

Heterogeneous charge transfer reaction





Electrode

Electrode

- Charge is transported through the electrode

  → by the movement of electrons (and holes).
- Typical electrode materials include

  → solid metals (e.g., Pt, Au), liquid metals (Hg, amalgams), carbon (graphite), and semiconductors (indium-tin oxide, Si).
- Two types of electrode

  → anode (negative electrode) and cathode (positive electrode)

$$\mathrm{O} + n\mathrm{e}^- \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} \mathrm{R}$$

Anode – electrode where oxidation (losing e^-) occurs

Cathode – electrode where reduction (accepting e^-) occurs

Electrolyte

Electrolyte

- In the electrolyte phase,

  → charge is carried by the movement of ions.

- To be useful in an electrochemical cell,

  → the electrolyte must have sufficiently low resistance

  (i.e., sufficiently ionically conductive)

  → indicating that the movement of ions is sufficiently fast

- The most common electrolytes

  : liquid solutions containing ionic species, such as, H^+, Na^+, Cl^-, in either water or a nonaqueous solvent.

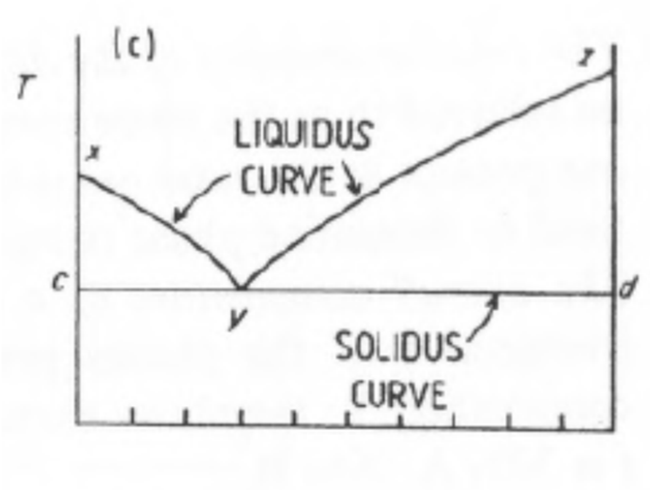
Electrolyte

- Less conventional electrolytes

  → fused salts (e.g., molten NaCl-KCl eutectic)

  → ionically conductive polymers (e.g., Nafion, polyethylene oxide-$LiClO_4$).

  → Solid electrolytes (e.g., sodium β-alumina, where charge is carried by mobile sodium ions that move between the aluminum oxide sheets)



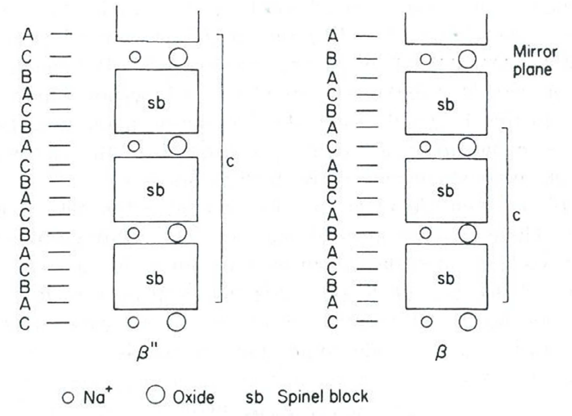


Fig. 7.24 Oxide packing in β- and β''-alumina

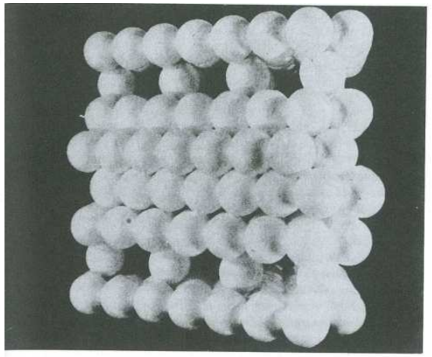


Fig. 7.23 Oxide layers in β-alumina

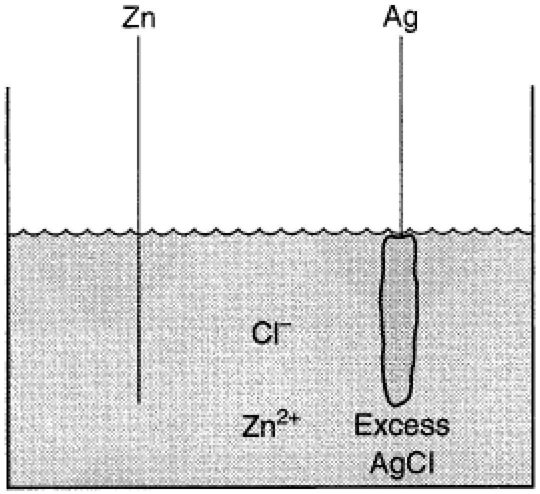
Electrochemical cell

- Generally defined as two electrodes separated by at least one electrolyte phase

- In general,
  → consider electrochemical events at a single interface
  → experimentally impossible
  → should study the properties of collections of interfaces called electrochemical cells

- A difference in electric potential (cell potential)
  → can be measured between the electrodes in an electrochemical cell

- Measure a potential difference with a high impedance voltmeter.



Electrochemical cell

- Measured in volts (V),

  → where 1 V = 1 joule/coulomb (J/C)

- 1 V

  → produce 1 J when 1 C of electrons pass through the external circuit

- This cell potential

  → is a measure of the energy available to drive charge externally between the electrodes

- The magnitude of the potential difference at an interface

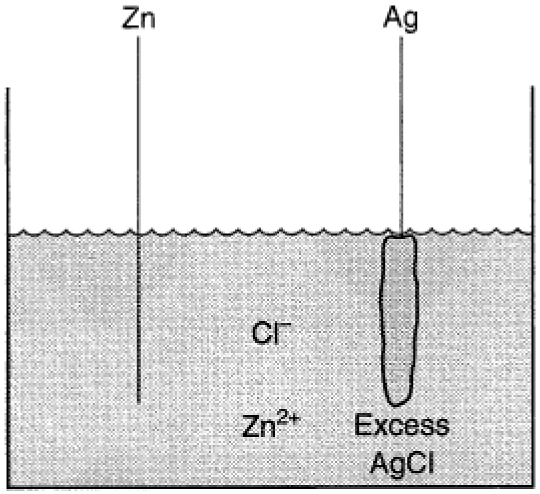
  → affects the relative energies of the charge carriers in the two phases

  → controls the direction and the rate of charge transfer.

  → the measurement and control of cell potential is one of the most important aspects of experimental electrochemistry.

Electrochemical cell

- A shorthand notation for expressing the structure of electrochemical cells



$Zn/Zn^{2+}, Cl^{-}/AgCl/Ag$

→ Slash: represents a phase boundary

→ Comma: separates two components in the same phase.

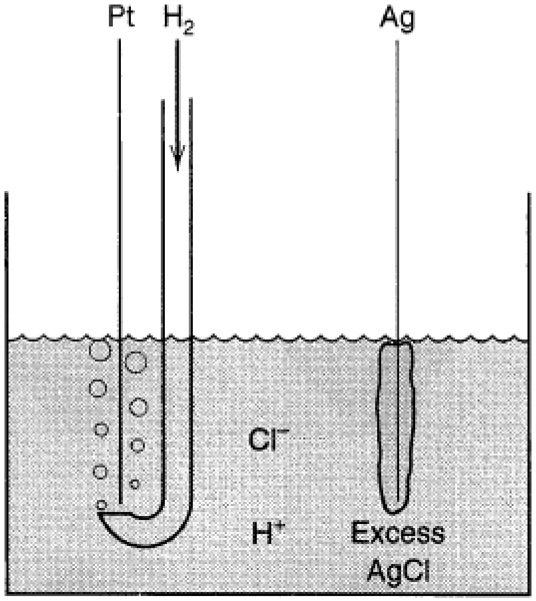
→ Double slash (not yet used here)

: represents a phase boundary whose potential is regarded as a negligible component of the overall cell potential.

Electrochemical cell

- When a gaseous phase is involved,

  → it is written adjacent to its corresponding conducting element.



$$Pt/H_2/H^+, Cl^-/AgCl/Ag$$

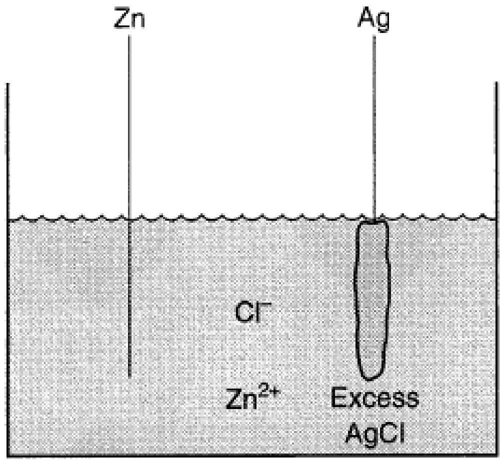
Electrochemical cell

- The overall chemical reaction taking place in a cell is made up of two independent half-reactions

→ Describe the real chemical changes at the two electrodes.

- Each half reaction (and, consequently, the chemical composition of the system near the electrodes)

→ responds to the interfacial potential difference at the corresponding electrode.

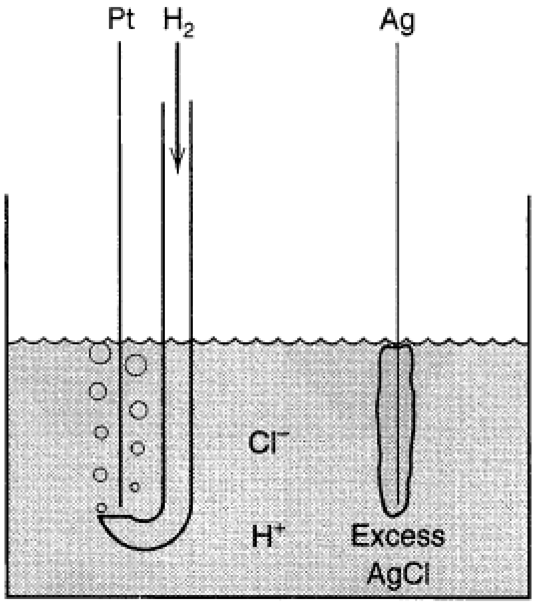


Anode half-reaction: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cathode half-reaction: $2AgCl(s) + 2e^- \longrightarrow 2Ag(s) + 2Cl^-(aq)$

Overall cell reaction: $Zn(s) + 2AgCl(s) \longrightarrow Zn^{2+}(aq) + 2Ag(s) + 2Cl^-(aq)$

Electrochemical cell



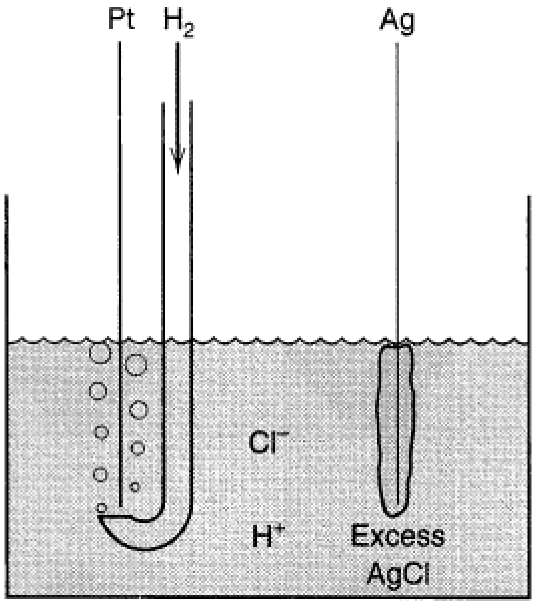
$Pt/H_2/H^+, Cl^-/AgCl/Ag$

Anode half-reaction:

Cathode half-reaction: $2AgCl(s) + 2e^- \longrightarrow 2Ag(s) + 2Cl^-(aq)$

Overall cell reaction:

Electrochemical cell



$Pt/H_2/H^+, Cl^-/AgCl/Ag$

Anode half-reaction: $H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

Cathode half-reaction: $2AgCl(s) + 2e^- \longrightarrow 2Ag(s) + 2Cl^-(aq)$

Overall cell reaction: $H_2(g) + 2AgCl(s) \longrightarrow 2H^+(aq) + 2Ag(s) + 2Cl^-(aq)$

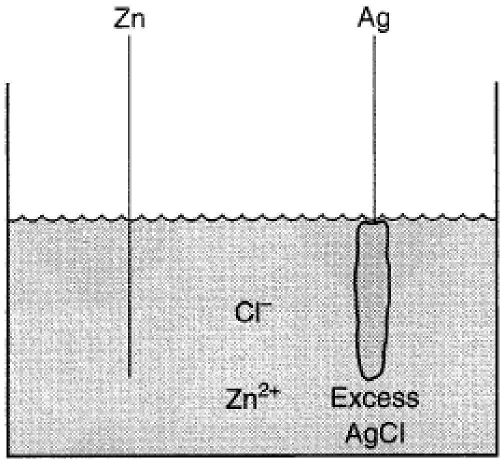
Working electrode

Working electrode

- Most of the time, one is interested in only one of the two independent half-reactions

→ The electrode at which it occurs is called the working electrode.

→ The other electrode is called the counter electrode



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Overall cell reaction: $Zn(s) + 2AgCl(s) \longrightarrow Zn^{2+}(aq) + 2Ag(s) + 2Cl^-(aq)$

Reference electrode

Reference electrode

- In order to easily compare with various electrochemical reactions at the working electrode,

→ one standardizes the other half of the cell (counter electrode) by using an electrode (called a reference electrode)

→ made up of phases having essentially constant composition.
(because composition affects a potential)

→ For more accurate measurement, counter and reference electrodes are experimentally separated

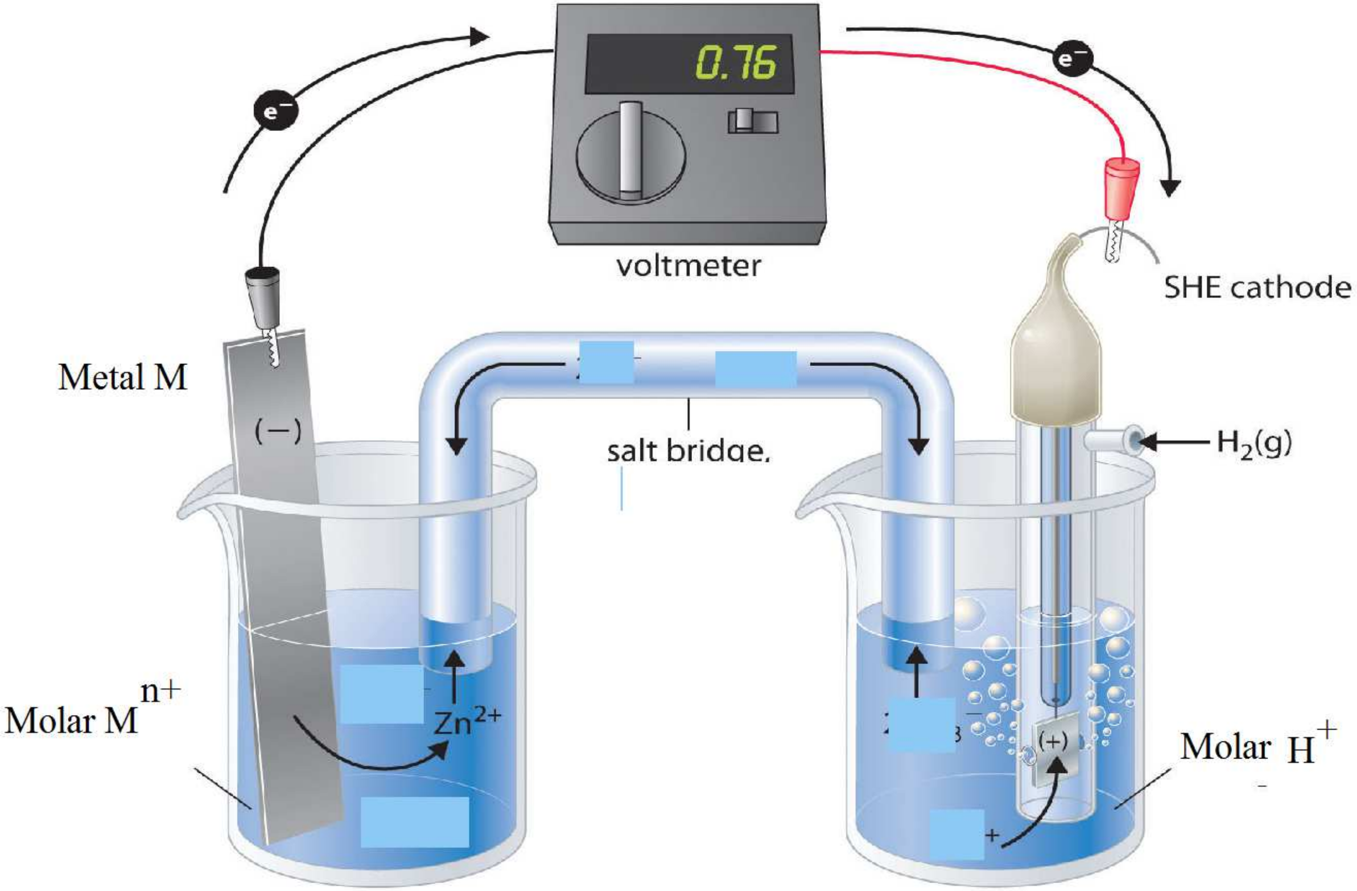
- The internationally accepted primary reference

→ the standard hydrogen electrode (SHE), or normal hydrogen electrode (NHE)

→ has all components at unit activity:

$$\mathrm{Pt/H_2}(a = 1)/\mathrm{H^+}(a = 1, \text{aqueous}) \qquad 2\,\mathrm{H^+(aq)} + 2\,e^- \leftrightarrow \mathrm{H_2(g)}$$

Reference electrode



Reference electrode

- Potentials are often measured with respect to reference electrodes other than the NHE

→ Because NHE is not very convenient from an experimental standpoint.

- A common reference

→ the saturated calomel electrode (SCE), which is

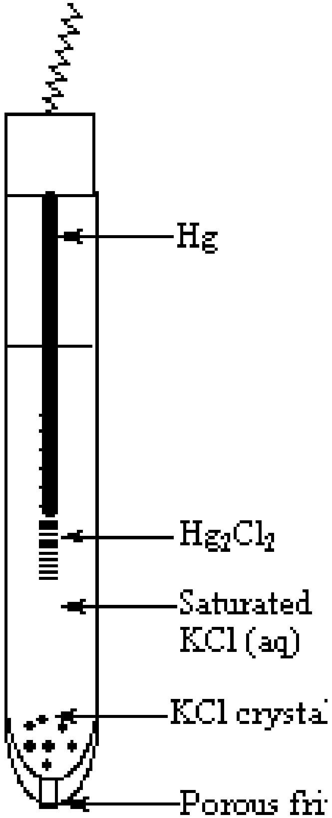
$$Hg/Hg_2Cl_2/KCl \text{ (saturated in water)}$$

→ the potential of SCE: 0.242 V vs. NHE.

$$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l)$$

$$Hg_2^{2+} + 2Cl^- \rightleftharpoons Hg_2Cl_2(s),$$

$$Hg_2Cl_2\,(s) + 2e^- \rightarrow 2\,Hg\,(s) + 2Cl^-\,(sat)$$



Reference electrode

- Another is the silver-silver chloride electrode,

Ag/AgCl/KCl (saturated in water)

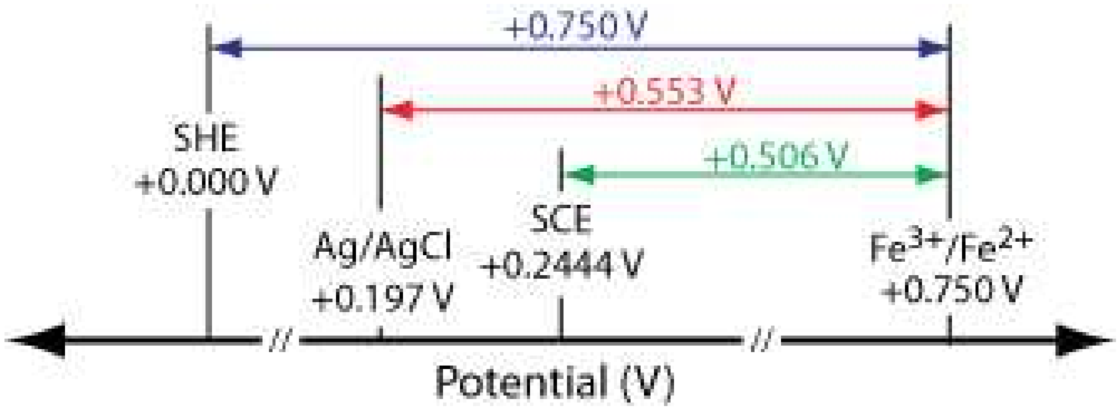
$$Ag^+ + e^- \rightleftharpoons Ag(s)$$

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$$

→ the potential of Ag/AgCl: 0.197 V vs. NHE.

→ Potentials identified in the literature as "vs. Ag/Ag⁺" when this electrode is used.



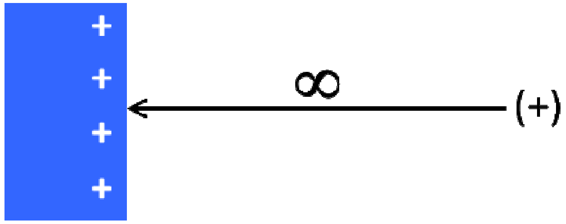
Charge transport: reduction

- Since the potential of the reference electrode is fixed, any changes in the cell are ascribable to the working electrode.

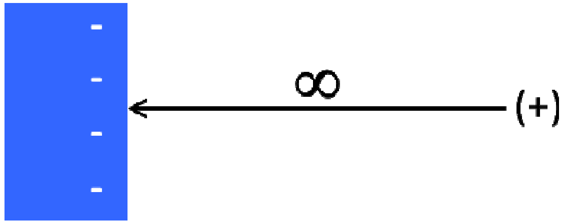
- When we control the potential of the working electrode with respect to the reference, it is equivalent to controlling the energy of the electrons within the working electrode

> “The **potential** at a point is the external work needed to bring a ***positive*** **unit charge (+)**, at constant speed, from the position of zero potential to the given point.”

University Physics, Harris Benson, Wiley



Positive Electrical potential



Negative Electrical potential

$$[\text{Electric potential}] = [V] = [A\cdot\Omega] = [J/C] = [N\cdot m/C] = [kg\cdot m^2/(C\cdot s^2)]$$

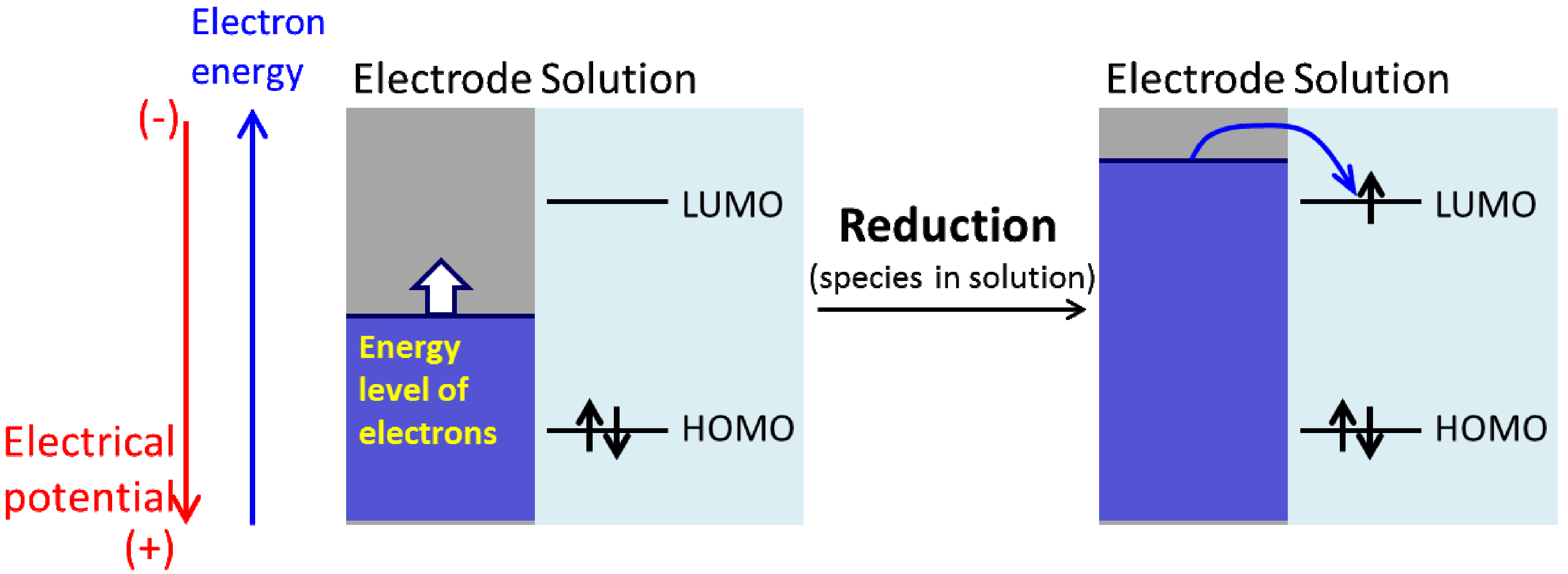
Charge transport: reduction

- By driving the electrode to more negative potentials using a power supply

→ The energy of the electrons is raised

→ They can reach a level high enough to transfer into vacant electronic states on species in the electrolyte

→ In that case, a flow of electrons from electrode to solution (a reduction current) occurs



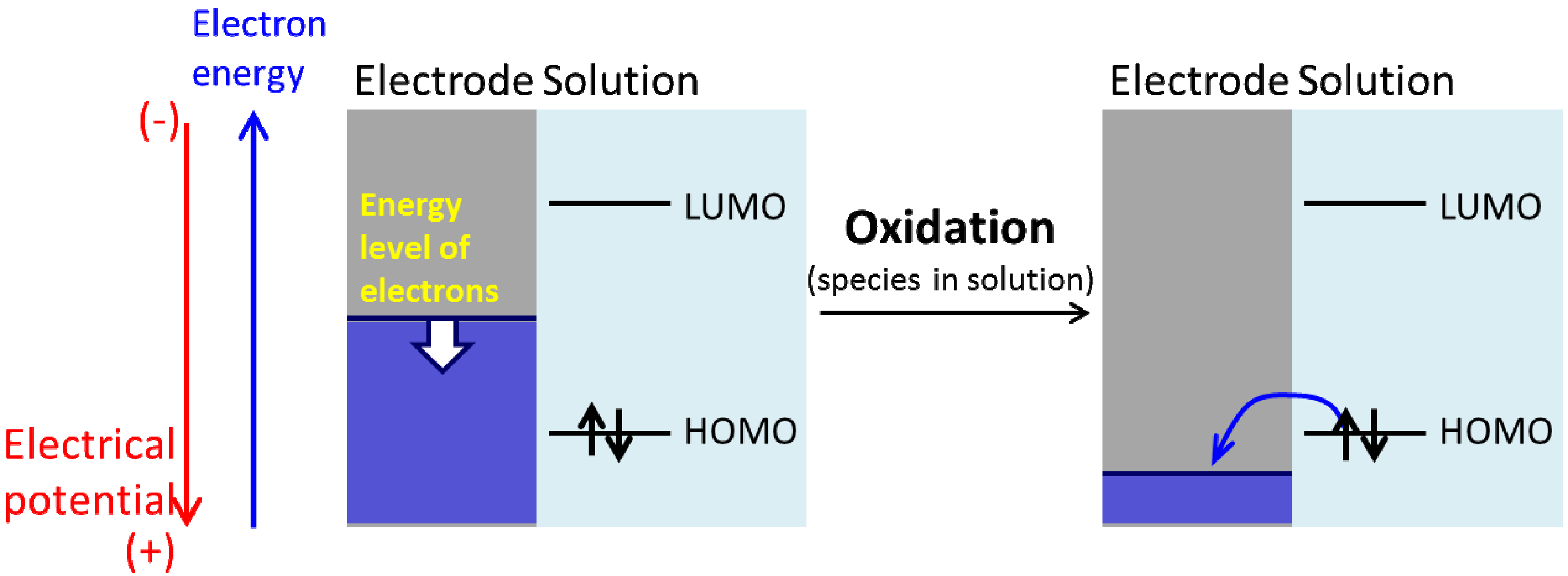
$$A + e \rightarrow A^-$$

Charge transport: oxidation

- Similarly, the energy of the electrons can be lowered by imposing a more positive potential

→ at some point, electrons on solutes in the electrolyte will transfer to a more stable energy on the electrode.

→ The electron flow from solution to electrode: oxidation current



$$A - e \rightarrow A^{+}$$

Standard electrode potentials

- The critical potentials at which these processes occur
  → related to the standard potentials, E°, for the specific chemical substances in the system.
  → Potentials at standard states (1M, 25°C)

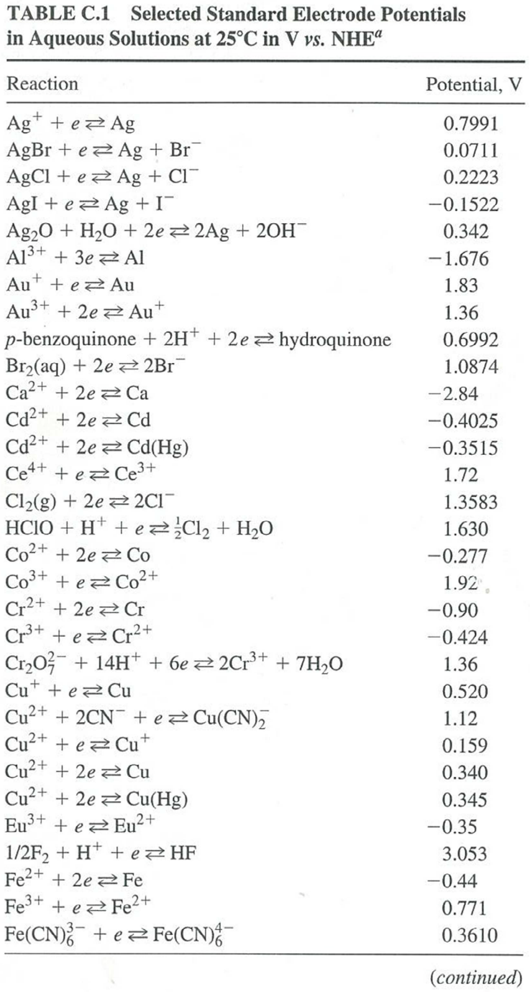


TABLE C.1 Selected Standard Electrode Potentials in Aqueous Solutions at 25°C in V *vs.* NHE[a]

Reaction	Potential, V
$Ag^+ + e \rightleftarrows Ag$	0.7991
$AgBr + e \rightleftarrows Ag + Br^-$	0.0711
$AgCl + e \rightleftarrows Ag + Cl^-$	0.2223
$AgI + e \rightleftarrows Ag + I^-$	−0.1522
$Ag_2O + H_2O + 2e \rightleftarrows 2Ag + 2OH^-$	0.342
$Al^{3+} + 3e \rightleftarrows Al$	−1.676
$Au^+ + e \rightleftarrows Au$	1.83
$Au^{3+} + 2e \rightleftarrows Au^+$	1.36
p-benzoquinone + $2H^+ + 2e \rightleftarrows$ hydroquinone	0.6992
$Br_2(aq) + 2e \rightleftarrows 2Br^-$	1.0874
$Ca^{2+} + 2e \rightleftarrows Ca$	−2.84
$Cd^{2+} + 2e \rightleftarrows Cd$	−0.4025
$Cd^{2+} + 2e \rightleftarrows Cd(Hg)$	−0.3515
$Ce^{4+} + e \rightleftarrows Ce^{3+}$	1.72
$Cl_2(g) + 2e \rightleftarrows 2Cl^-$	1.3583
$HClO + H^+ + e \rightleftarrows \frac{1}{2}Cl_2 + H_2O$	1.630
$Co^{2+} + 2e \rightleftarrows Co$	−0.277
$Co^{3+} + e \rightleftarrows Co^{2+}$	1.92
$Cr^{2+} + 2e \rightleftarrows Cr$	−0.90
$Cr^{3+} + e \rightleftarrows Cr^{2+}$	−0.424
$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftarrows 2Cr^{3+} + 7H_2O$	1.36
$Cu^+ + e \rightleftarrows Cu$	0.520
$Cu^{2+} + 2CN^- + e \rightleftarrows Cu(CN)_2^-$	1.12
$Cu^{2+} + e \rightleftarrows Cu^+$	0.159
$Cu^{2+} + 2e \rightleftarrows Cu$	0.340
$Cu^{2+} + 2e \rightleftarrows Cu(Hg)$	0.345
$Eu^{3+} + e \rightleftarrows Eu^{2+}$	−0.35
$1/2F_2 + H^+ + e \rightleftarrows HF$	3.053
$Fe^{2+} + 2e \rightleftarrows Fe$	−0.44
$Fe^{3+} + e \rightleftarrows Fe^{2+}$	0.771
$Fe(CN)_6^{3-} + e \rightleftarrows Fe(CN)_6^{4-}$	0.3610

(*continued*)

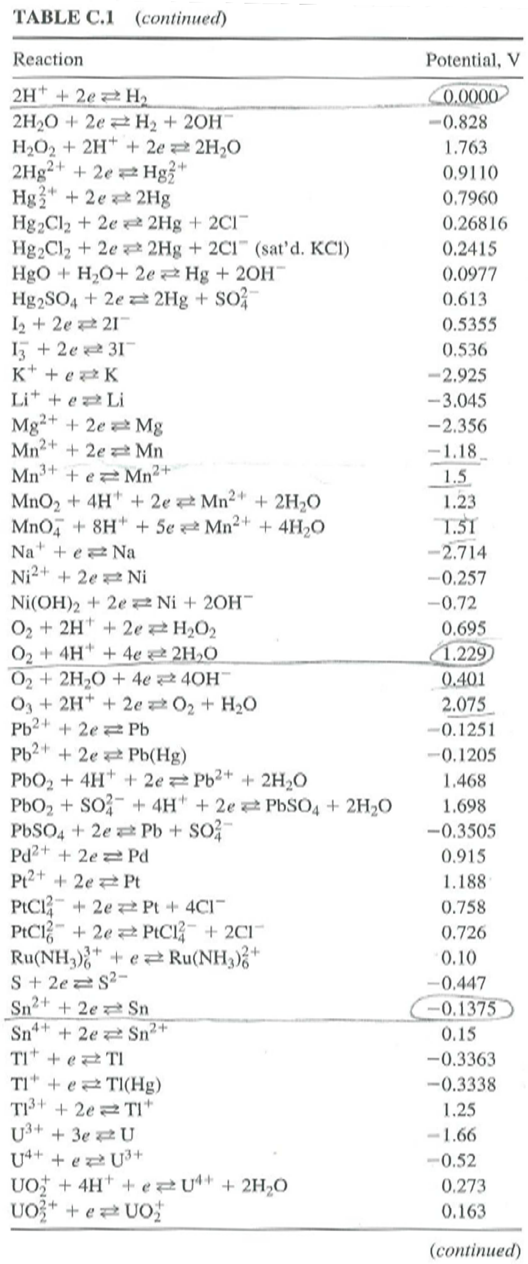


TABLE C.1 (*continued*)

Reaction	Potential, V
$2H^+ + 2e \rightleftarrows H_2$	0.0000
$2H_2O + 2e \rightleftarrows H_2 + 2OH^-$	−0.828
$H_2O_2 + 2H^+ + 2e \rightleftarrows 2H_2O$	1.763
$2Hg^{2+} + 2e \rightleftarrows Hg_2^{2+}$	0.9110
$Hg_2^{2+} + 2e \rightleftarrows 2Hg$	0.7960
$Hg_2Cl_2 + 2e \rightleftarrows 2Hg + 2Cl^-$	0.26816
$Hg_2Cl_2 + 2e \rightleftarrows 2Hg + 2Cl^-$ (sat'd. KCl)	0.2415
$HgO + H_2O + 2e \rightleftarrows Hg + 2OH^-$	0.0977
$Hg_2SO_4 + 2e \rightleftarrows 2Hg + SO_4^{2-}$	0.613
$I_2 + 2e \rightleftarrows 2I^-$	0.5355
$I_3^- + 2e \rightleftarrows 3I^-$	0.536
$K^+ + e \rightleftarrows K$	−2.925
$Li^+ + e \rightleftarrows Li$	−3.045
$Mg^{2+} + 2e \rightleftarrows Mg$	−2.356
$Mn^{2+} + 2e \rightleftarrows Mn$	−1.18
$Mn^{3+} + e \rightleftarrows Mn^{2+}$	1.5
$MnO_2 + 4H^+ + 2e \rightleftarrows Mn^{2+} + 2H_2O$	1.23
$MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{2+} + 4H_2O$	1.51
$Na^+ + e \rightleftarrows Na$	−2.714
$Ni^{2+} + 2e \rightleftarrows Ni$	−0.257
$Ni(OH)_2 + 2e \rightleftarrows Ni + 2OH^-$	−0.72
$O_2 + 2H^+ + 2e \rightleftarrows H_2O_2$	0.695
$O_2 + 4H^+ + 4e \rightleftarrows 2H_2O$	1.229
$O_2 + 2H_2O + 4e \rightleftarrows 4OH^-$	0.401
$O_3 + 2H^+ + 2e \rightleftarrows O_2 + H_2O$	2.075
$Pb^{2+} + 2e \rightleftarrows Pb$	−0.1251
$Pb^{2+} + 2e \rightleftarrows Pb(Hg)$	−0.1205
$PbO_2 + 4H^+ + 2e \rightleftarrows Pb^{2+} + 2H_2O$	1.468
$PbO_2 + SO_4^{2-} + 4H^+ + 2e \rightleftarrows PbSO_4 + 2H_2O$	1.698
$PbSO_4 + 2e \rightleftarrows Pb + SO_4^{2-}$	−0.3505
$Pd^{2+} + 2e \rightleftarrows Pd$	0.915
$Pt^{2+} + 2e \rightleftarrows Pt$	1.188
$PtCl_4^{2-} + 2e \rightleftarrows Pt + 4Cl^-$	0.758
$PtCl_6^{2-} + 2e \rightleftarrows PtCl_4^{2-} + 2Cl^-$	0.726
$Ru(NH_3)_6^{3+} + e \rightleftarrows Ru(NH_3)_6^{2+}$	0.10
$S + 2e \rightleftarrows S^{2-}$	−0.447
$Sn^{2+} + 2e \rightleftarrows Sn$	−0.1375
$Sn^{4+} + 2e \rightleftarrows Sn^{2+}$	0.15
$Tl^+ + e \rightleftarrows Tl$	−0.3363
$Tl^+ + e \rightleftarrows Tl(Hg)$	−0.3338
$Tl^{3+} + 2e \rightleftarrows Tl^+$	1.25
$U^{3+} + 3e \rightleftarrows U$	−1.66
$U^{4+} + e \rightleftarrows U^{3+}$	−0.52
$UO_2^+ + 4H^+ + e \rightleftarrows U^{4+} + 2H_2O$	0.273
$UO_2^{2+} + e \rightleftarrows UO_2^+$	0.163

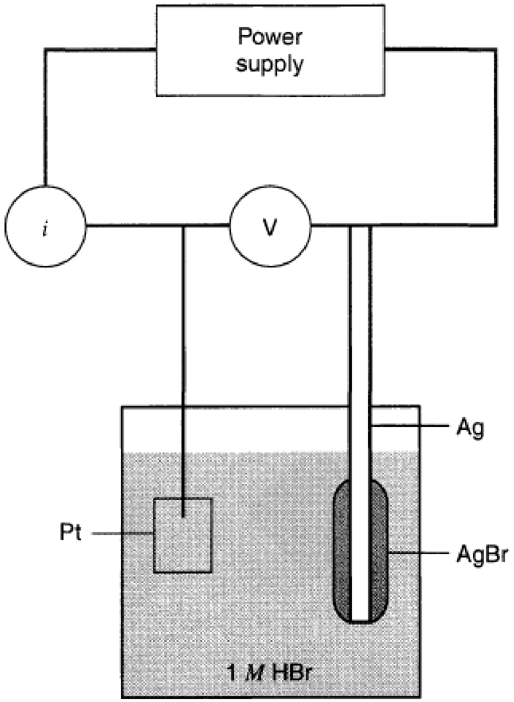
(*continued*)

Number of electrons

- Consider a typical electrochemical experiment where a working electrode and a reference electrode are immersed in a solution

➔ We measure a potential across the cell using a high impedance voltmeter

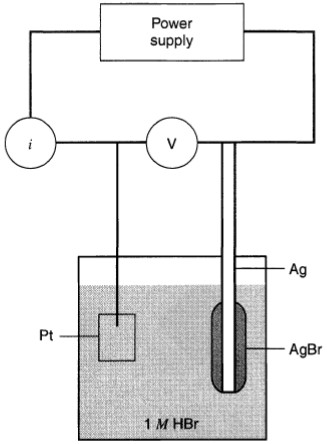
➔ called the open-circuit potential of the cell because the internal resistance of the voltammeter is so high that no appreciable current flows through it during a measurement



- The potential difference between the electrodes can be varied by means of an external power supply

- This variation in potential, E, can produce a current flow in the external circuit, because electrons cross the electrode/solution interfaces as electrochemical reactions occur.

Number of electrons



- The number of electrons that cross an interface

  : stoichiometrically proportional to the extent of the chemical reaction

  (i.e., to the amounts of reactant consumed and product generated).

➔ The number of electrons is measured in terms of the total charge, Q, passed in the circuit.

➔ Unit of charge: coulombs (C), where 1 C = 6.24 X 10^{18} electrons.

➔ **Faraday's law**

: relationship between charge and amount of product formed

: the passage of 96,485.4 C → 1 mole of reaction for a one-electron reaction.

: 1 mole = 6.02 X 10^{23}

Current

- Current, i

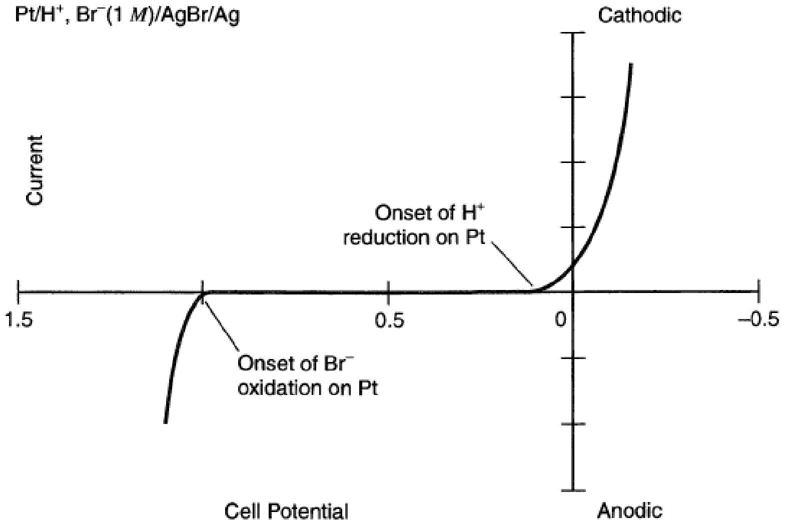
  : the rate of flow of coulombs (or electrons)

  : unit of a current = ampere (A)

  : 1 A = 1 C/s.

- When one plots the current as a function of the potential, one obtains a current-potential (i vs. E) curve.

→ information about the nature of the solution and the electrodes and about the reactions that occur at the interfaces.



Electrochemical reaction

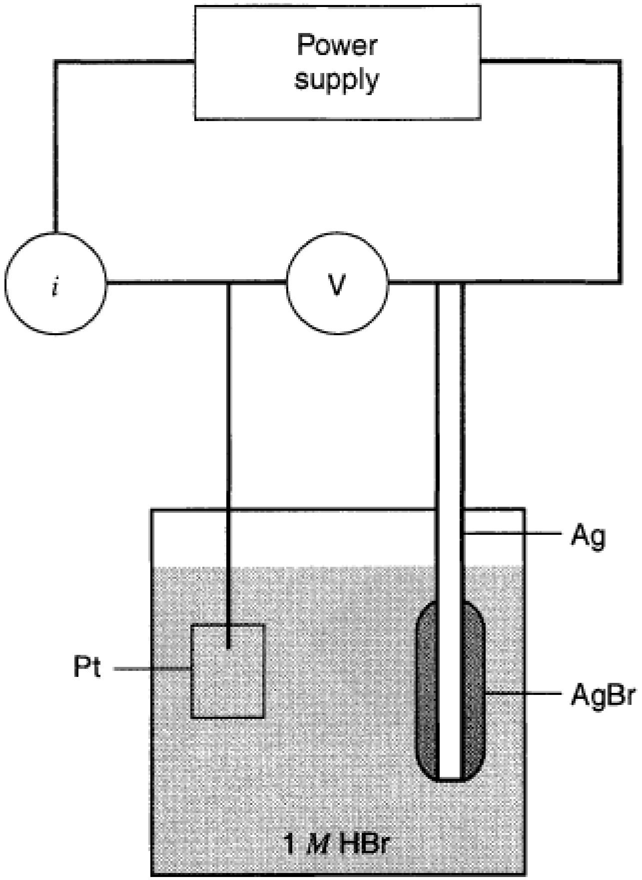
- Let us now consider that a power supply, a voltmeter and a microammeter are connected across the cell

- composed of the Pt working electrode and the Ag/AgBr reference electrode.

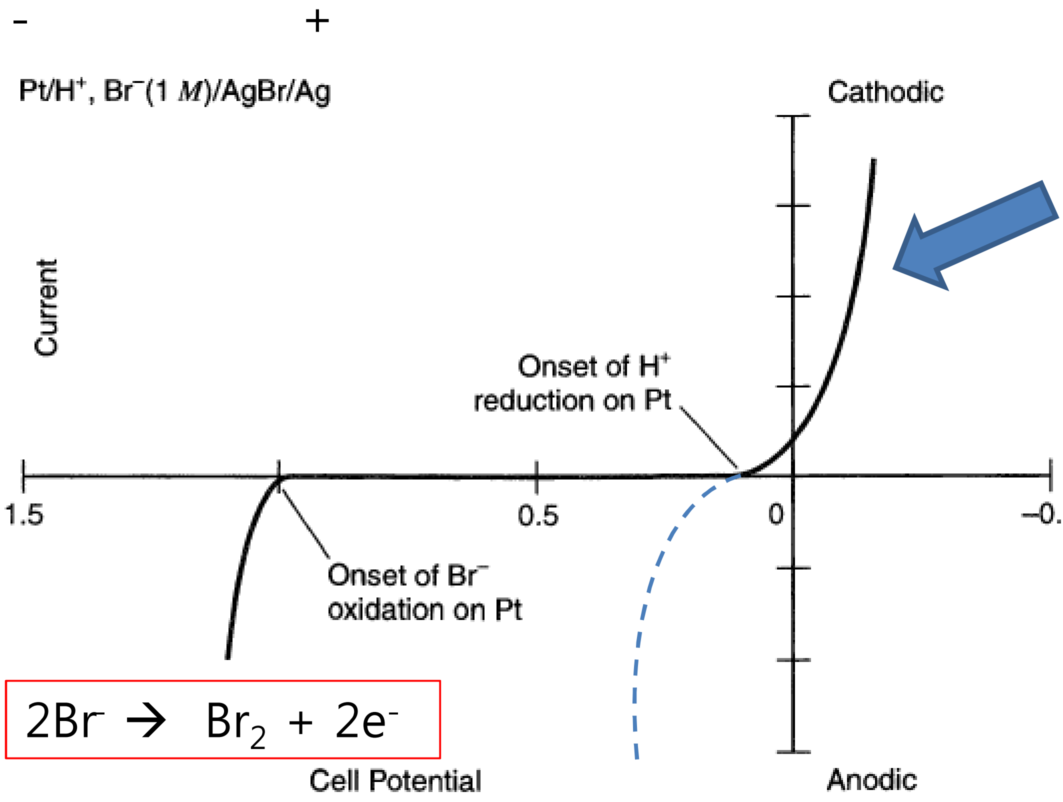
- As we gradually decrease the potential of the working electrode, the electrochemical reaction occurs (current flows)

➔ reduction of protons (hydrogen evolution)

➔ current-potential curve



I vs V curve



$2Br^- \rightarrow Br_2 + 2e^-$

Schematic current-potential curve for the cell Pt/H⁺, Br⁻ (1*M*)/AgBr/Ag

- Direction of electron flow

  : from the electrode to protons in solution

  ➔ cathodic current

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

- Sign convention

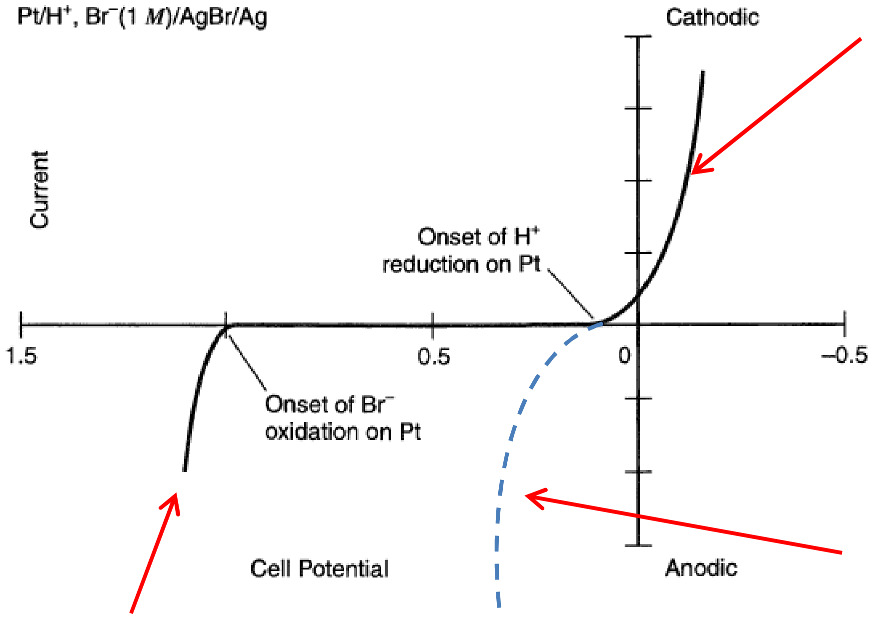
  : cathodic currents are taken as positive

- the onset of current flow occurs when the potential of the Pt electrode is near 0 V vs. NHE or -0.07 V vs. the Ag/AgBr electrode

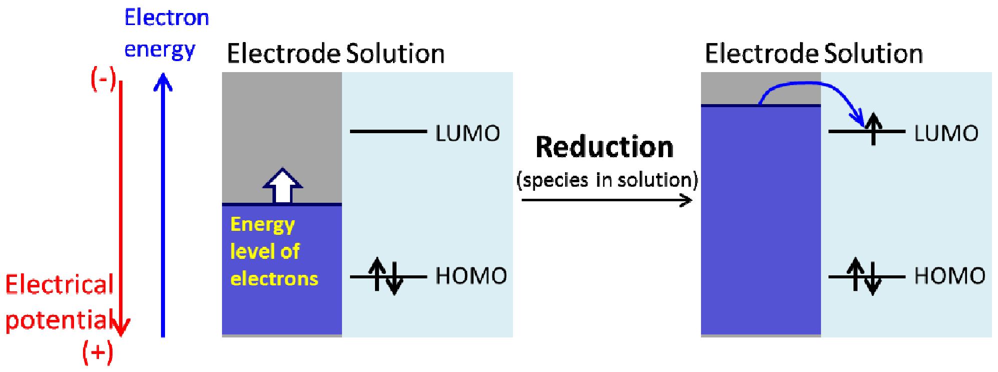
  ➔ Electrochemical potential for the H^+/H_2 reaction

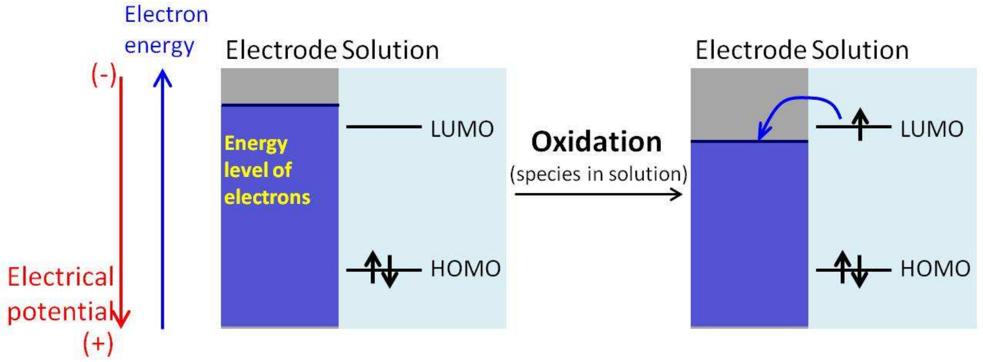
I vs V curve

Schematic current-potential curve for the cell Pt/H^+, Br^- (1*M*)/AgBr/Ag



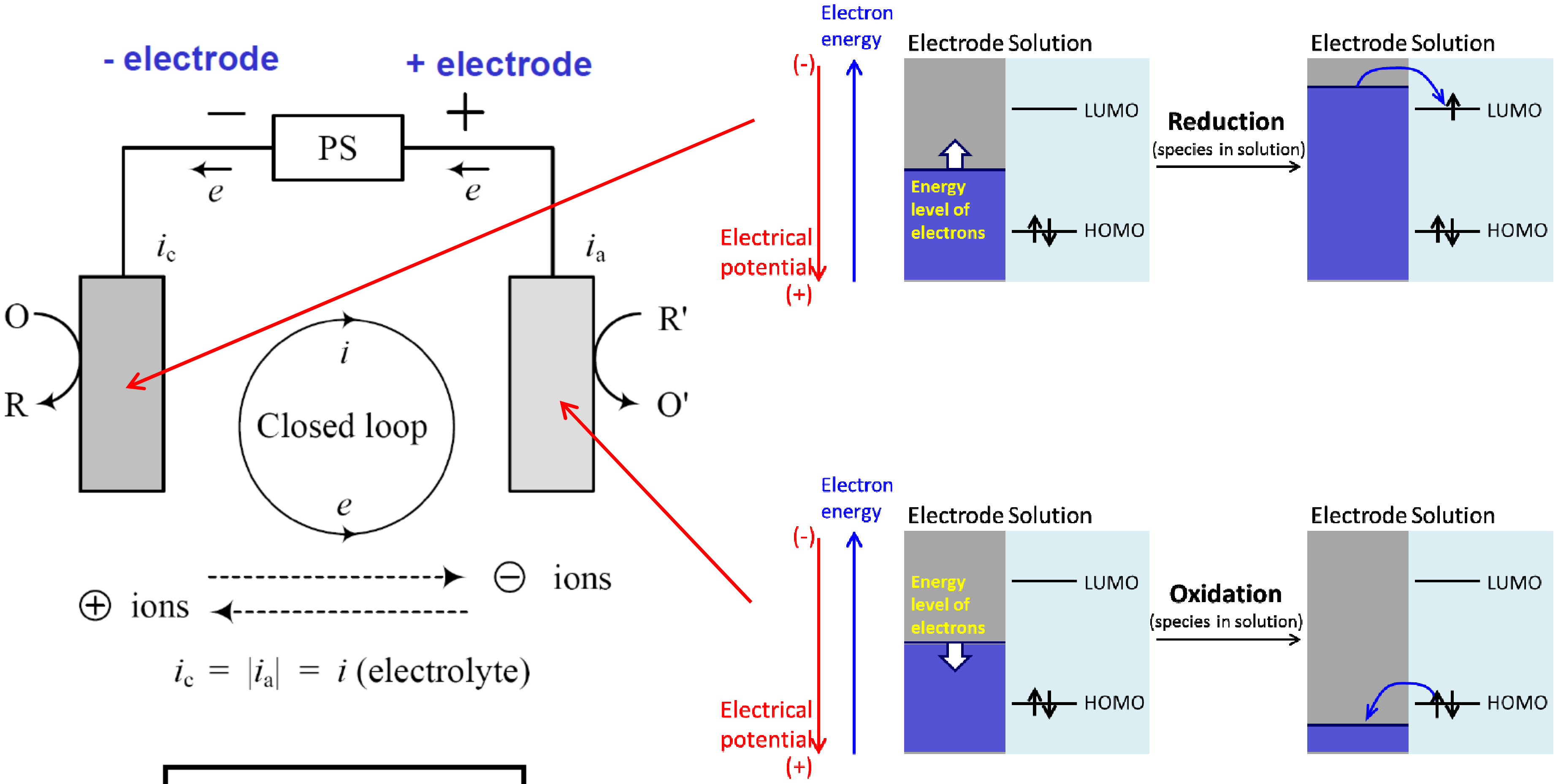
$2Br^- \rightarrow Br_2 + 2e^-$





- If H_2 gas is fed into solution, the oxidation of H_2 should be observed
- Anodic current: negative sign

Current passes through “closed loop”



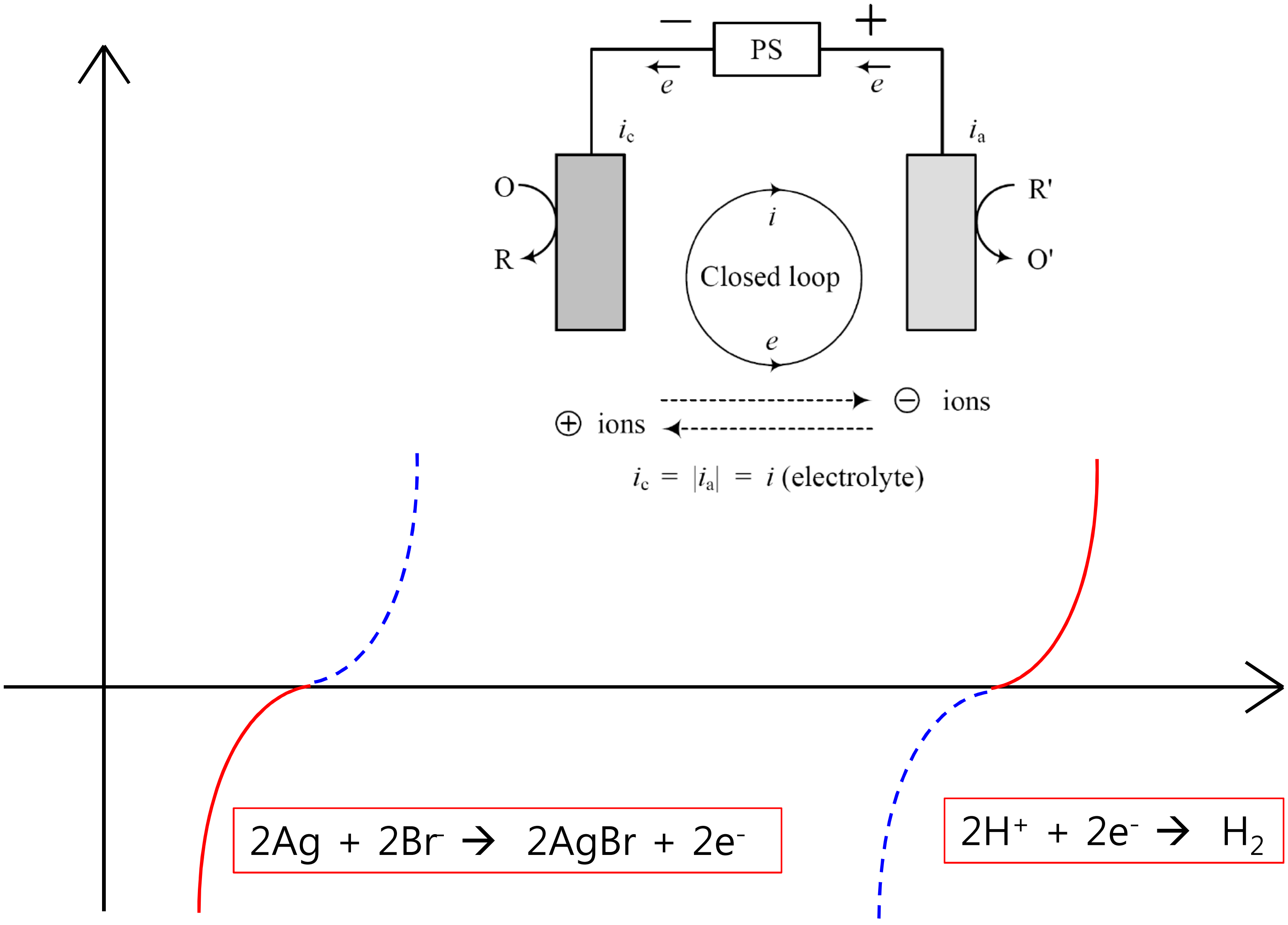
$$i_c = |i_a| = i \text{ (electrolyte)}$$

i_c: cathodic current

i_a : anodic current

- The oxidation of Ag to form AgBr at the counter electrode

Current passes through “closed loop”



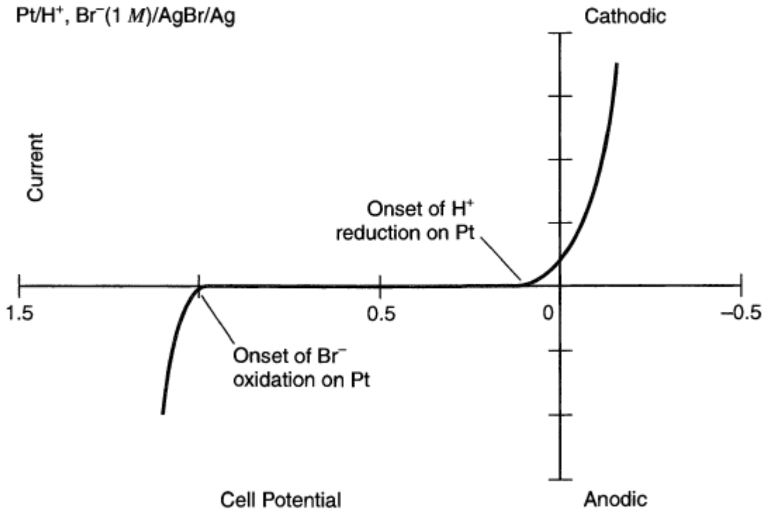
$2Ag + 2Br^- \rightarrow 2AgBr + 2e^-$

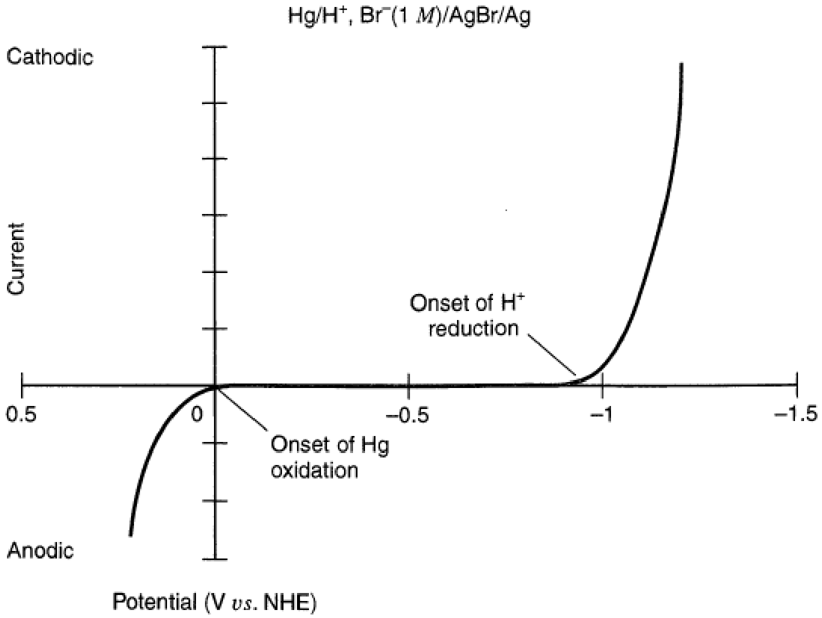
$2H^+ + 2e^- \rightarrow H_2$

at the counter electrode

at the working electrode

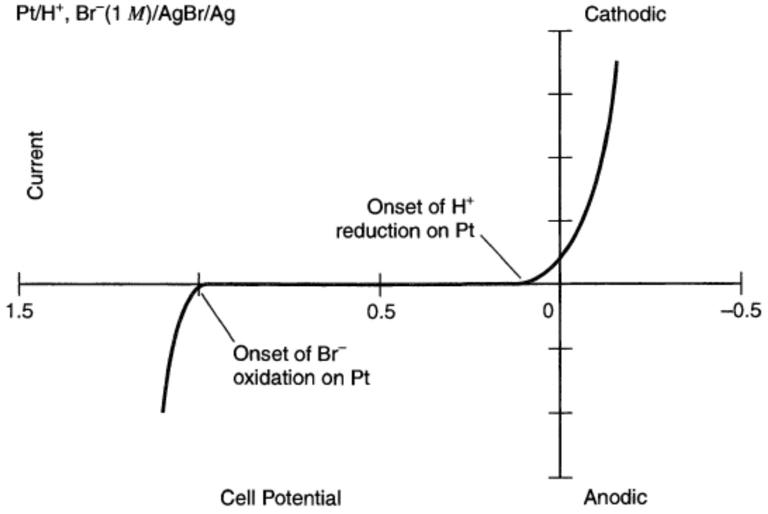
Overpotential

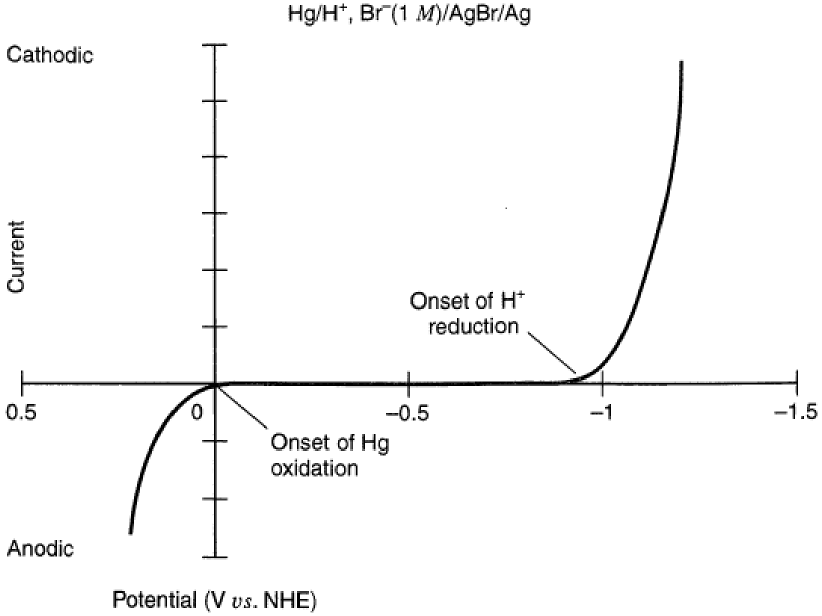




- Let us compare with two different working electrodes such as Pt and Hg
- The onset potential of Hg is more negative value despite of that the thermodynamics have not changed, since the half-reaction (hydrogen evolution) is independent of the metal electrode

Overpotential





- Considerably higher electron energies (more negative potentials) must be applied to make the reaction occur on the Hg electrode
- The additional potential (beyond the thermodynamic requirement) needed to drive a reaction at a certain rate is called the overpotential.

➔ it is said that mercury shows "a high overpotential for the hydrogen evolution reaction."