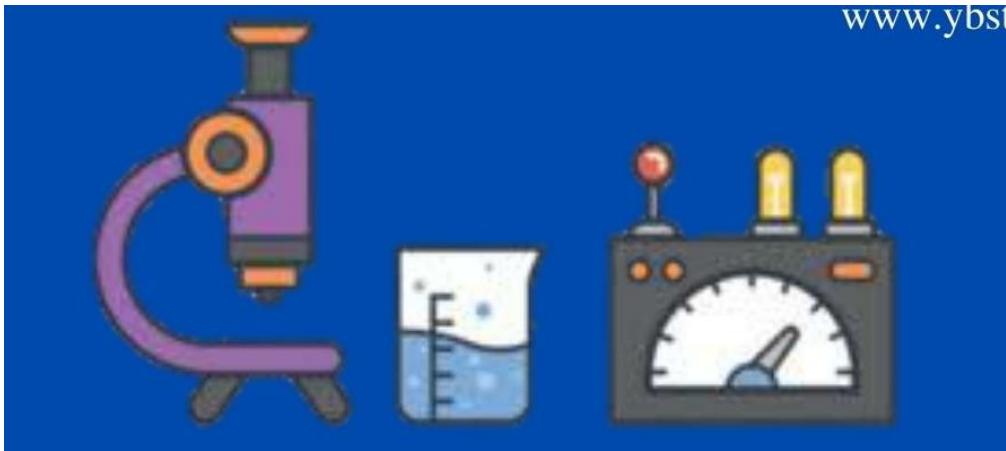


CO-1: Electrochemistry

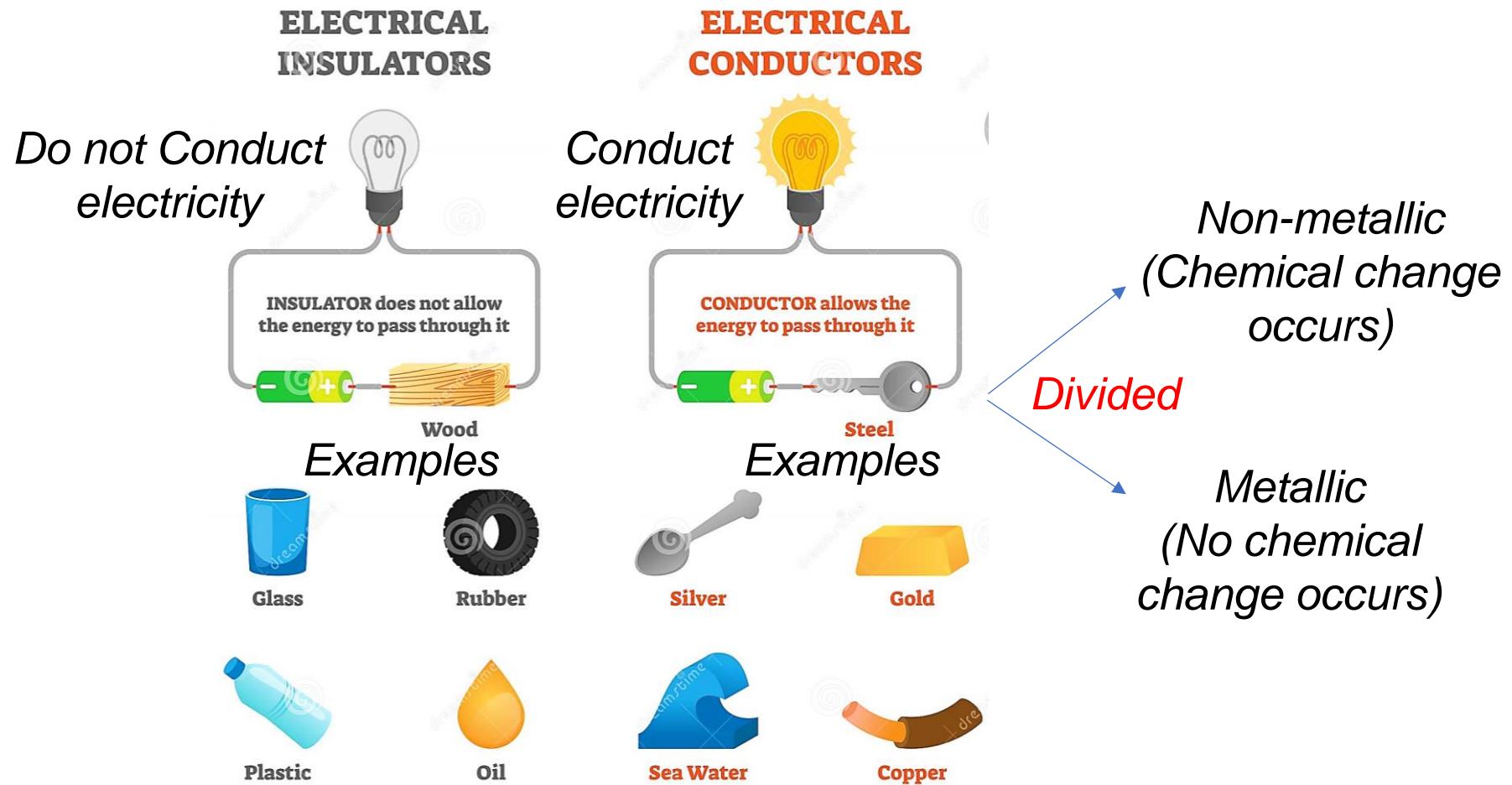


Electrochemistry

Department of Chemistry
Koneru Lakshmaiah Education Foundation (**KLEF**)

Introduction

- The behavior of electric current varies depending on the substance.

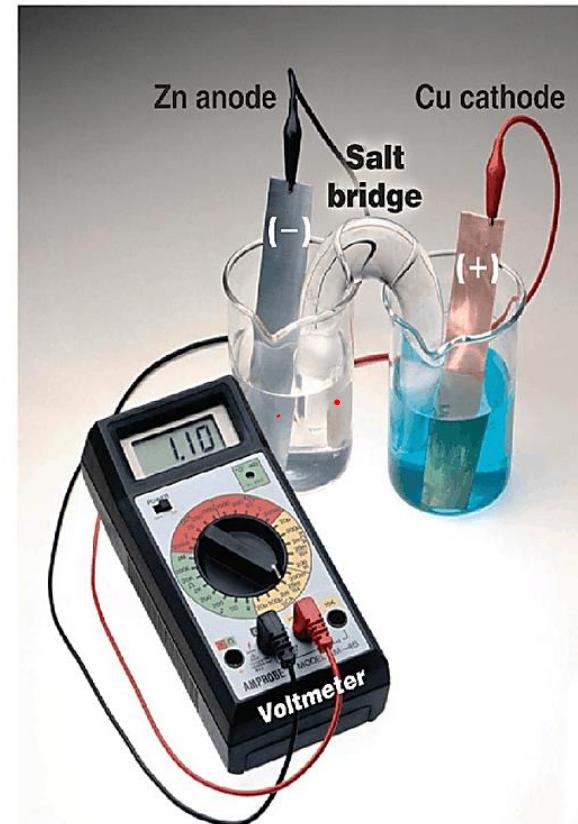
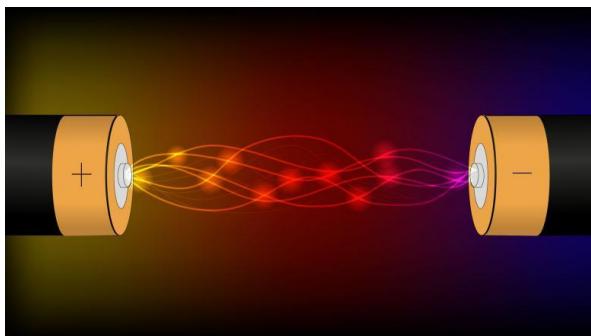


Introduction

☞ **Electrochemistry** is the study of chemical reactions that take place at the interface of an electrode and the electrolyte.

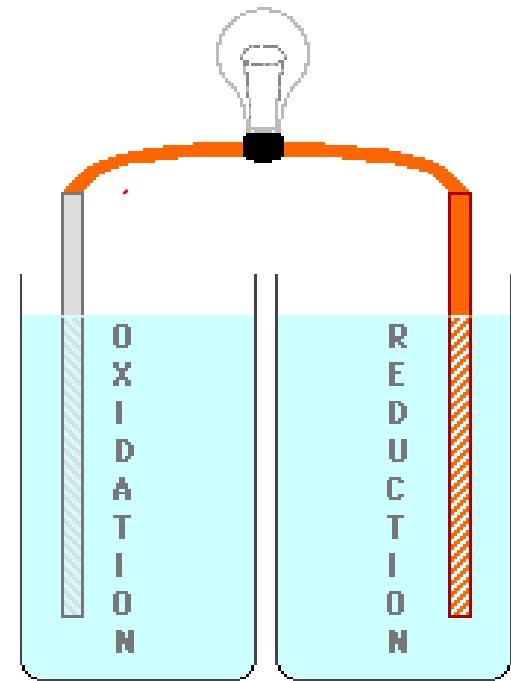
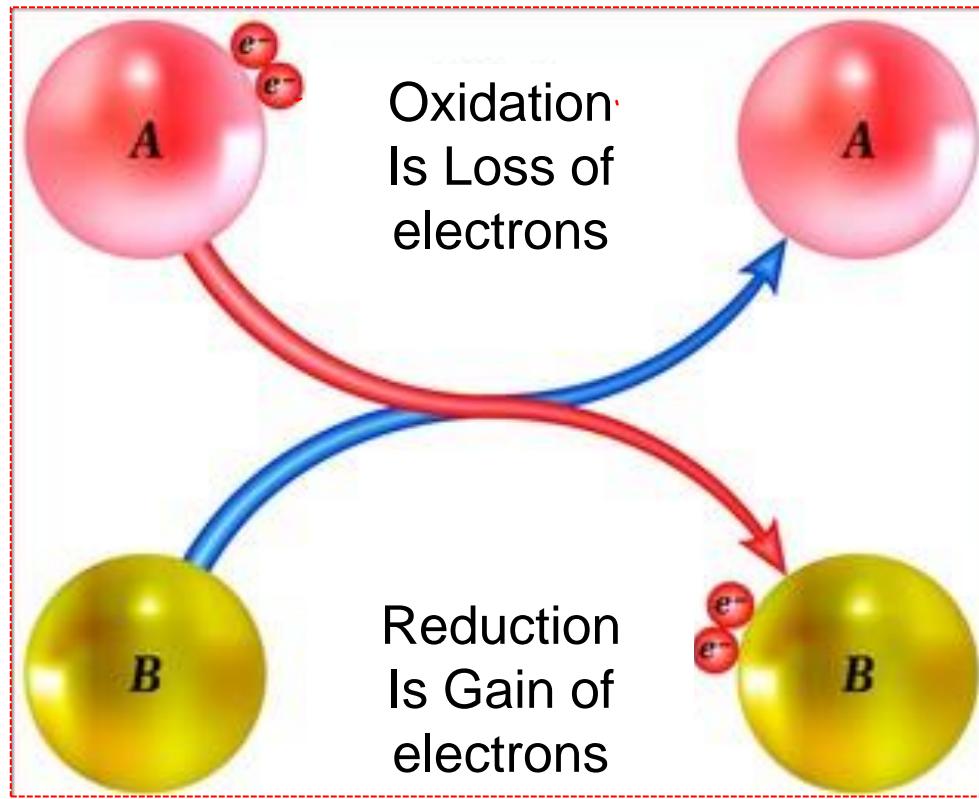
☞ Is the study of how electricity affects chemical reactions.

☞ It deals with the interaction between electrical energy & chemical change.



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Electrochemical reactions (ERs)



*Chemical reactions that involve the **input or generation** of electric currents are called ERs.*

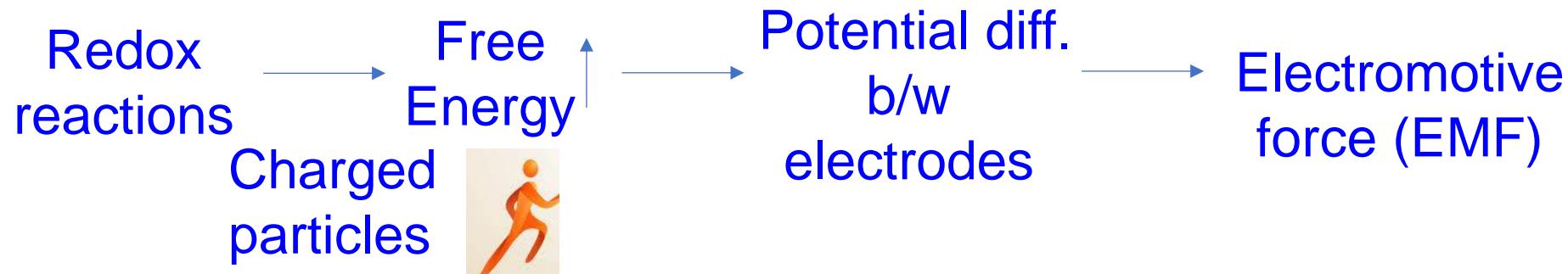
Electrochemical cells

Is a **device** consisting of two electrodes, each in contact with a solution of its **own ions** & transforms the free energy change of the redox reaction at the electrodes into **electrical energy**.



- It is filled with an ionic solution.
- Providing a pathway for ion transfer
- It is to allow for free flow of electrons from one solution to the other.

Electrochemical cells



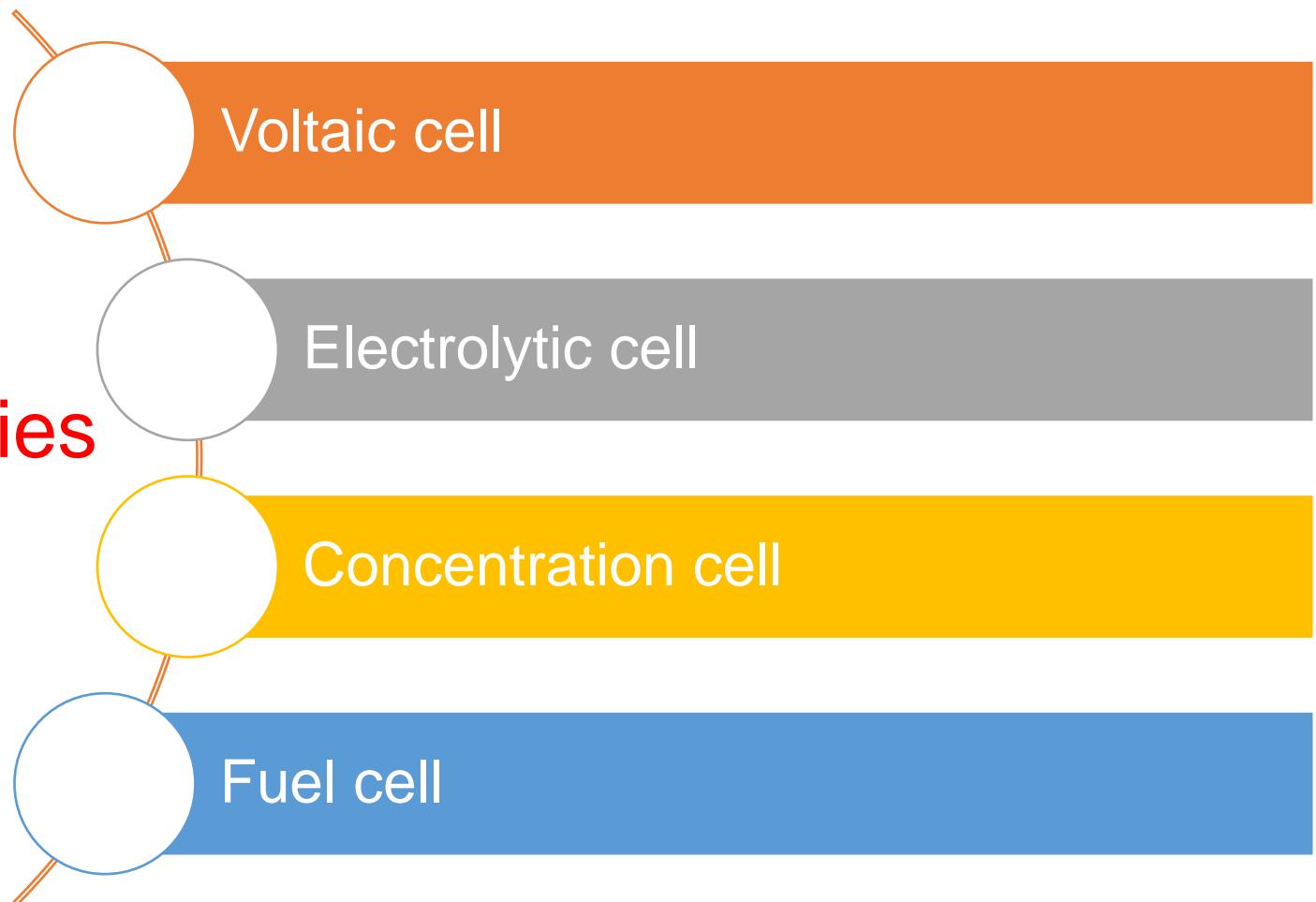
ECs work by converting free energy from redox reactions into electrical energy.

$$\text{i.e., } \Delta G = -nFE$$

More +V, the greater the tendency for the reaction to proceed to spontaneity.

Electrochemical cells

Categories



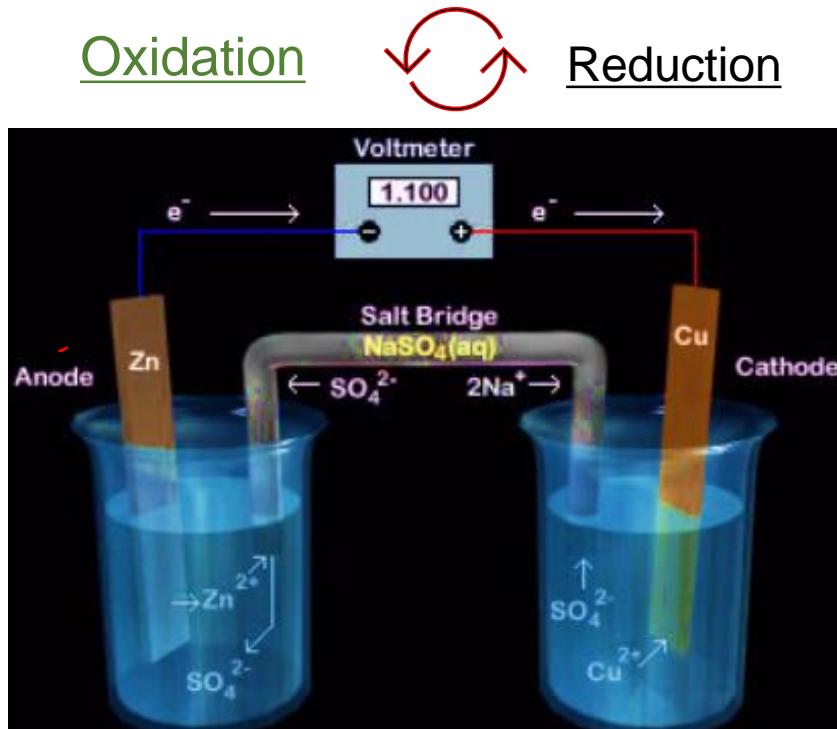
Electrochemical cells



Voltaic cell

It uses a **chemical reaction** to produce electrical energy.

- Spontaneous redox reaction
- Produces electricity
- Composed of two half-cells
- Different container
- e-s migrate Anode to cathode in external circuit



E.g.,



Lead storage cell

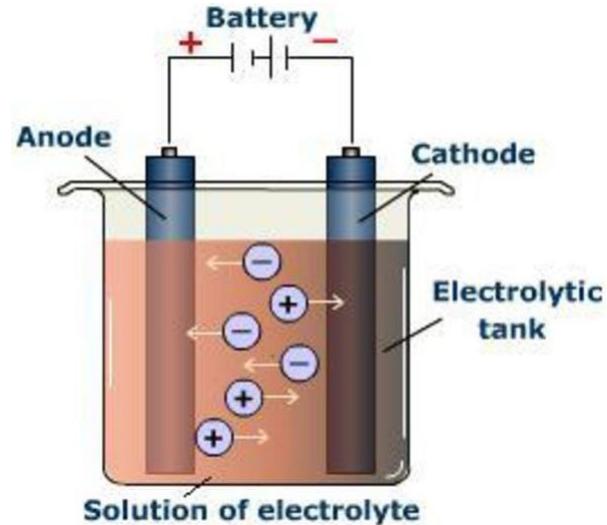


Dry cell

Electrochemical cells



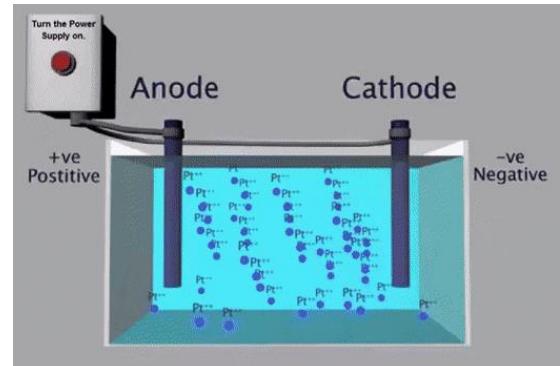
Electrolytic cell



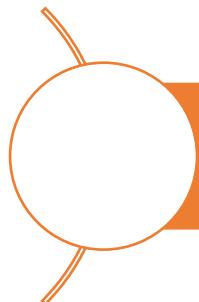
- It is device in which electrical energy from an external source can be used to produce chemical reactions.
- Energy is absorbed to drive non-spontaneous redox reaction.
- Electrical energy into Chemical energy.

Applications:

- Refining metal,
- Electroplating.



Electrochemical cells

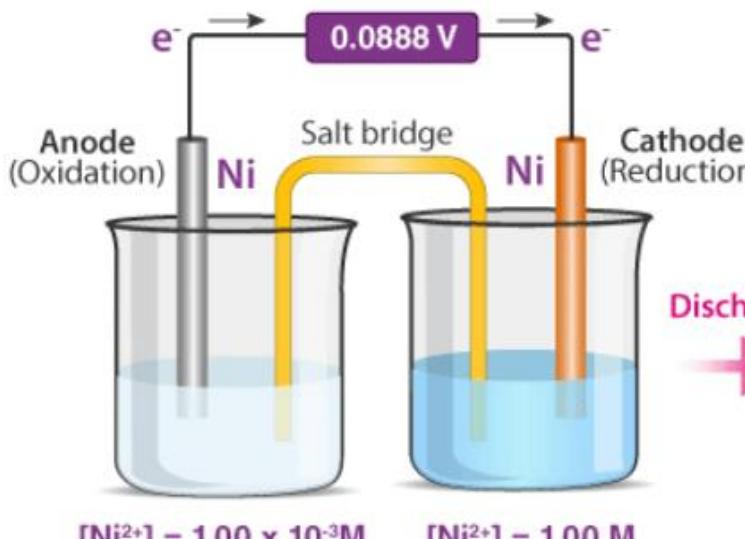


Concentration cell

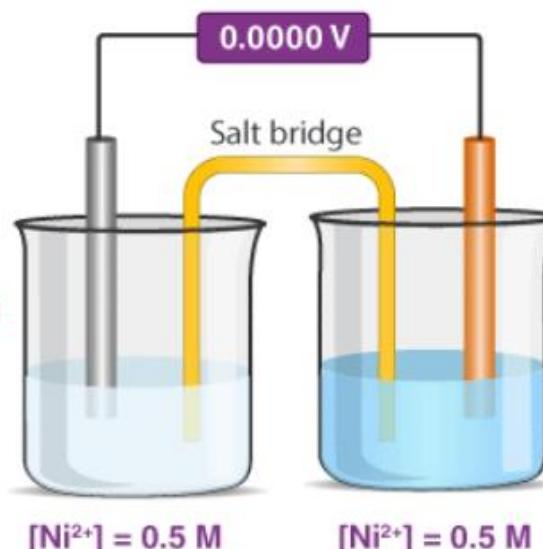


Is also an electrochemical device that generates electrical energy when two electrodes of the **same metal** are in contact with solutions of its **ions at different concentrations**.

to establish chemical equilibrium



Discharge

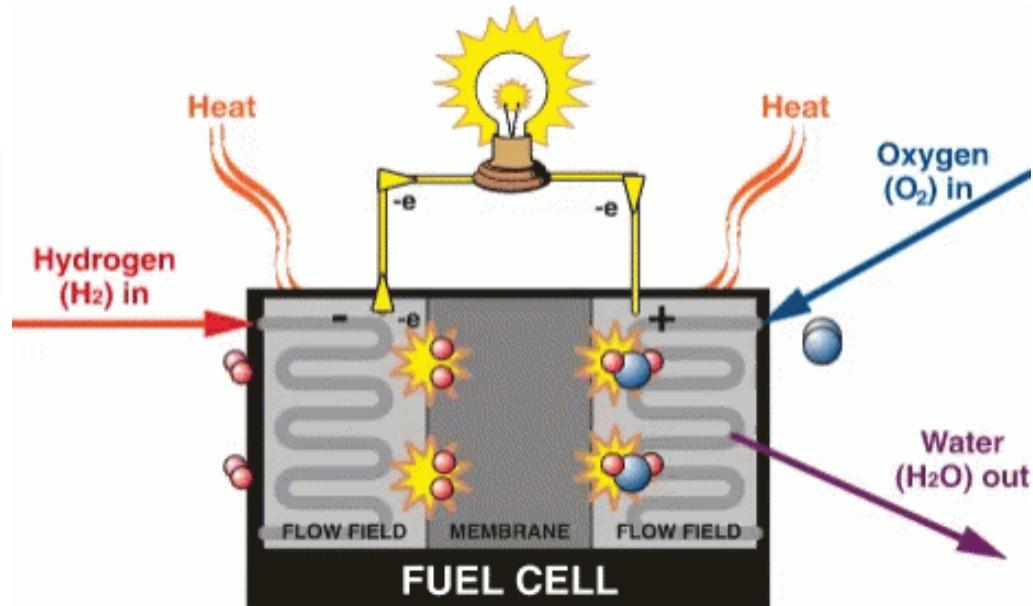


lower concentration

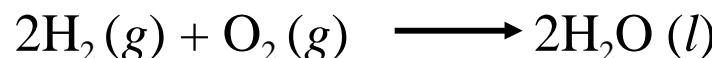
Electrochemical cells



Fuel cell

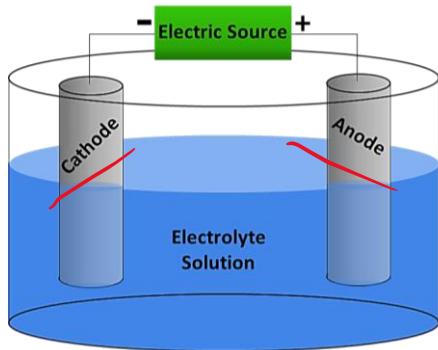


👉 Is also an electrochemical device that converts the chemical energy of a fuel and an oxidizing agent into electricity through a pair of redox reactions.



Difference b/w Galvanic and Electrolytic Cell

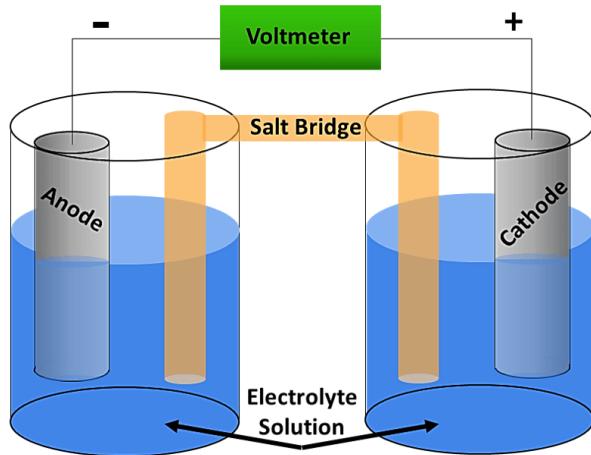
Electrolytic cell



- Convert electrical into chemical energy.
- Non-spontaneous redox reaction.
- Electrodes are of dissimilar or same metals.
- Immersed in same solution.
- No salt bridge is needed.

Electrical to chemical

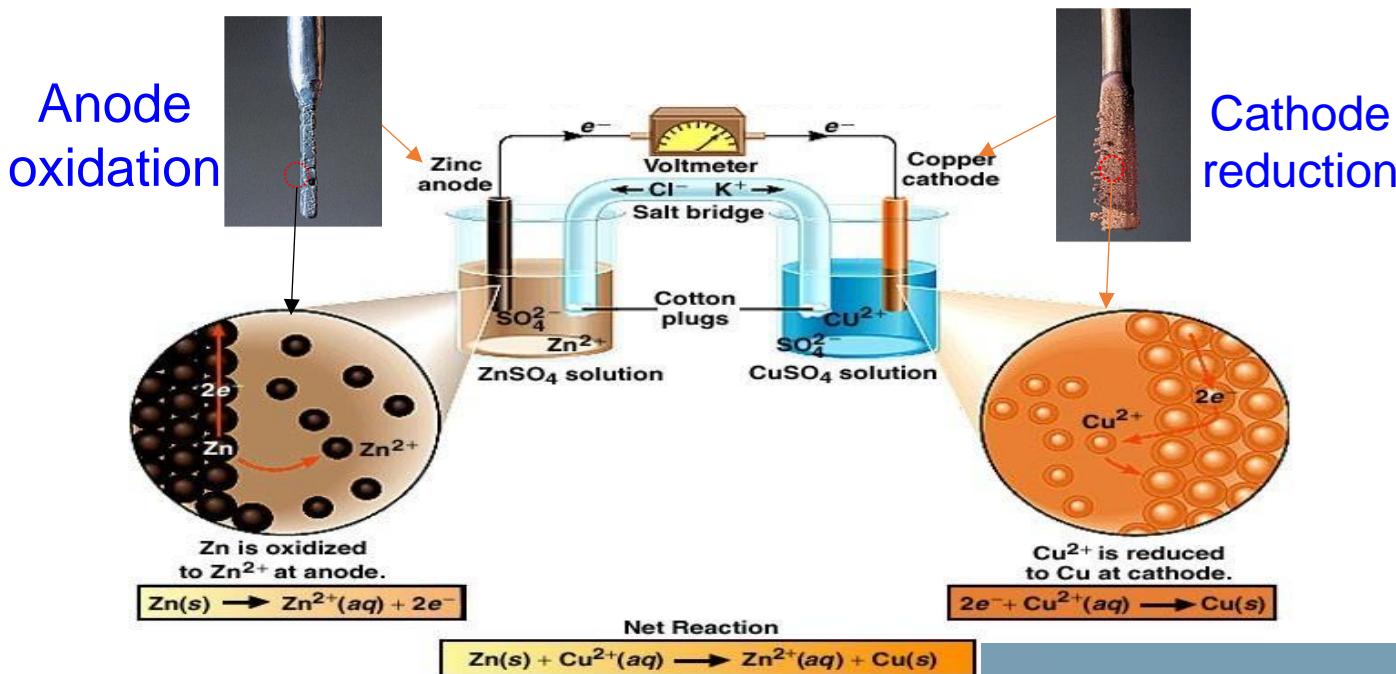
Galvanic (Voltaic) cell



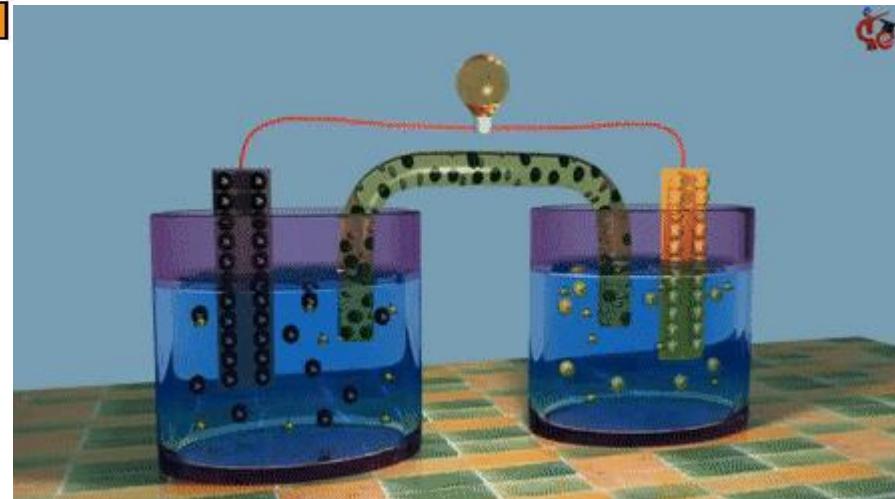
Chemical to electrical

- Convert chemical into electrical energy
- Spontaneous redox reaction
- Produces electricity
- Electrodes are of dissimilar metals.
- Composed of two half-cells
- They are connected by a salt bridge.

A Galvanic cell



Daniel cell is the best example of a galvanic cell



Electrochemical cell notation/line notation

.....is a shorthand method of expressing a certain reaction in an electrochemical cell

- Anode
- Cathode
- Salt Bridge
- Single line: show phase boundaries
- Two line: represent liquid junction

components of
anode compartment
(oxidation half-cell)

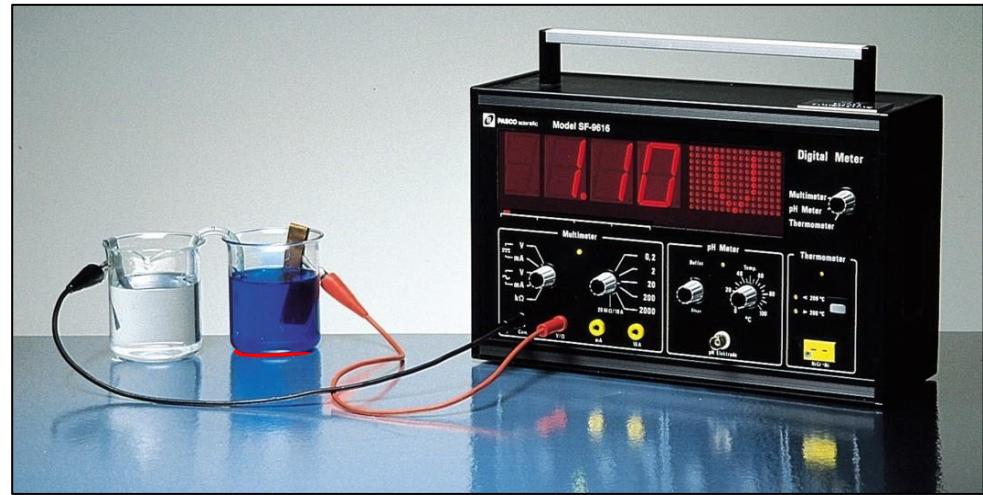
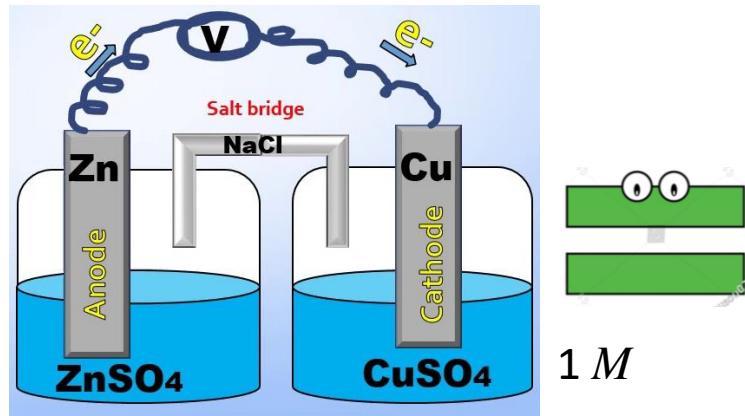
components of
cathode compartment
(reduction half-cell)



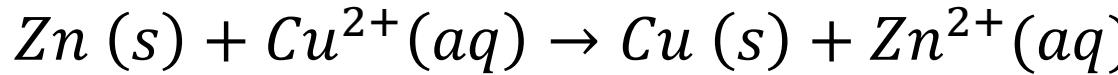
Cell notation:

Anode | anode solution // cathode solution| Cathode

Electrochemical cell notation/line notation



Cell Notation



Anode

Cathode

More detail..

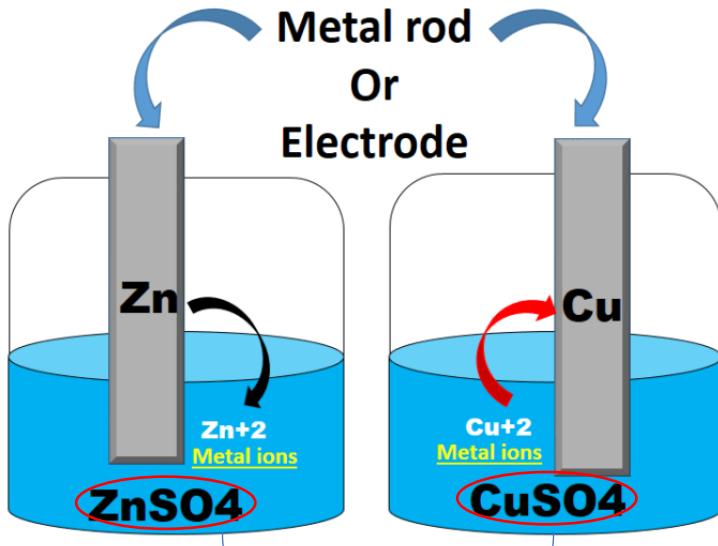


Anode

Salt bridge

Cathode

Single electrode potential



Its own salts

At oxidation;
(anode)

☞ Metal ions pass into solution.
 $Zn \rightarrow Zn^{+2} + ne^-$; the sign of the EP is +ve

$$E_{M^{n+}/M}^{\circ} = +ve$$

At Reduction
(cathode)

☞ Metal ions get deposited over the metal.
 $Cu^{+2} + ne^- \rightarrow Cu$ the sign of the EP is -ve

$$E_{M^{n+}/M}^{\circ} = -ve$$

Standard Electrode Potentials (SEP)

- ✓ Electrode potential of a cell depends concentrations and system temperature.
- ✓ Thus, potentials of different substances must be measured under standard conditions.

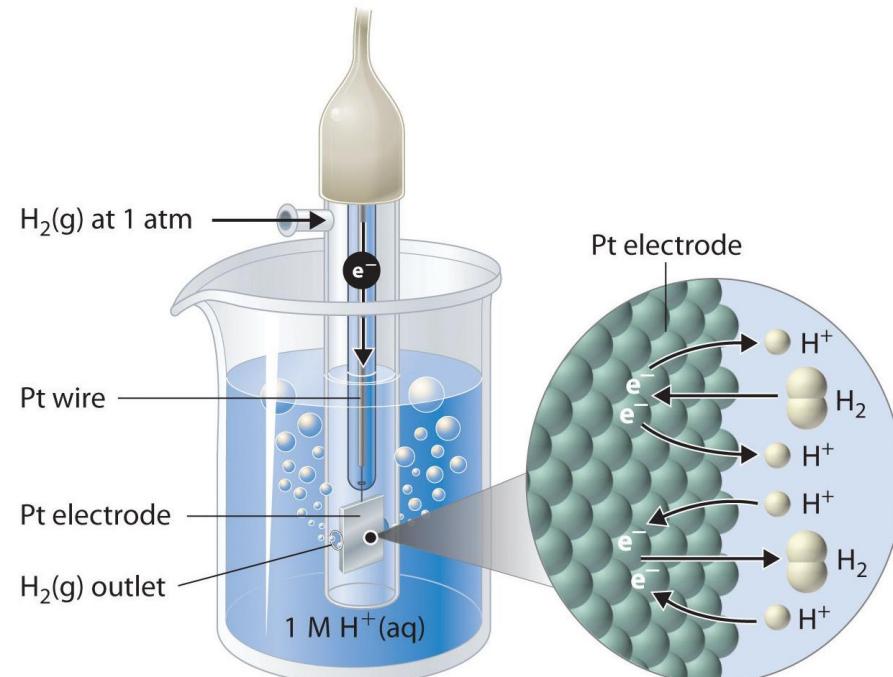
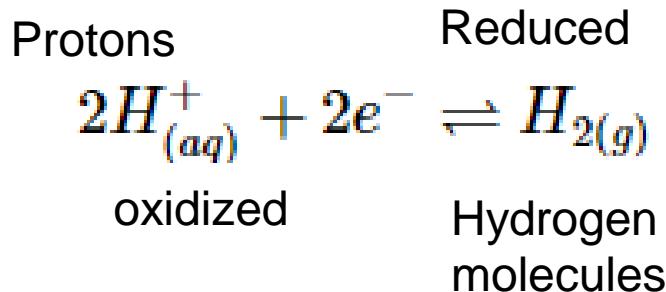
SEP (E_{cell}^o) is defined as the potential of an electrode measured under standard conditions of 298 K, 1 atm, & 1 M concentration.

$$E_{cell}^o = E_{cathode \ (reduction)}^o - E_{anode \ (oxidation)}^o$$

The overall cell reaction is the sum of the two half-reactions, but the cell potential is the difference between the reduction potentials:

Standard Electrode Potentials (SEP)

- The potential of given metal or nonmetal cannot be measured directly, so we must select a reference electrode whose potential is defined as 0 V.
- The **standard hydrogen electrode (SHE)** is universally used for this purpose.



SHE has the advantage of not consuming the Pt metal electrode.

*half-reaction at Pt surface:
 $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$*

Determining an unknown $E^\circ_{\text{half-cell}}$ with the standard reference (hydrogen) electrode

The potential of a half-reaction measured against the SHE under standard conditions.

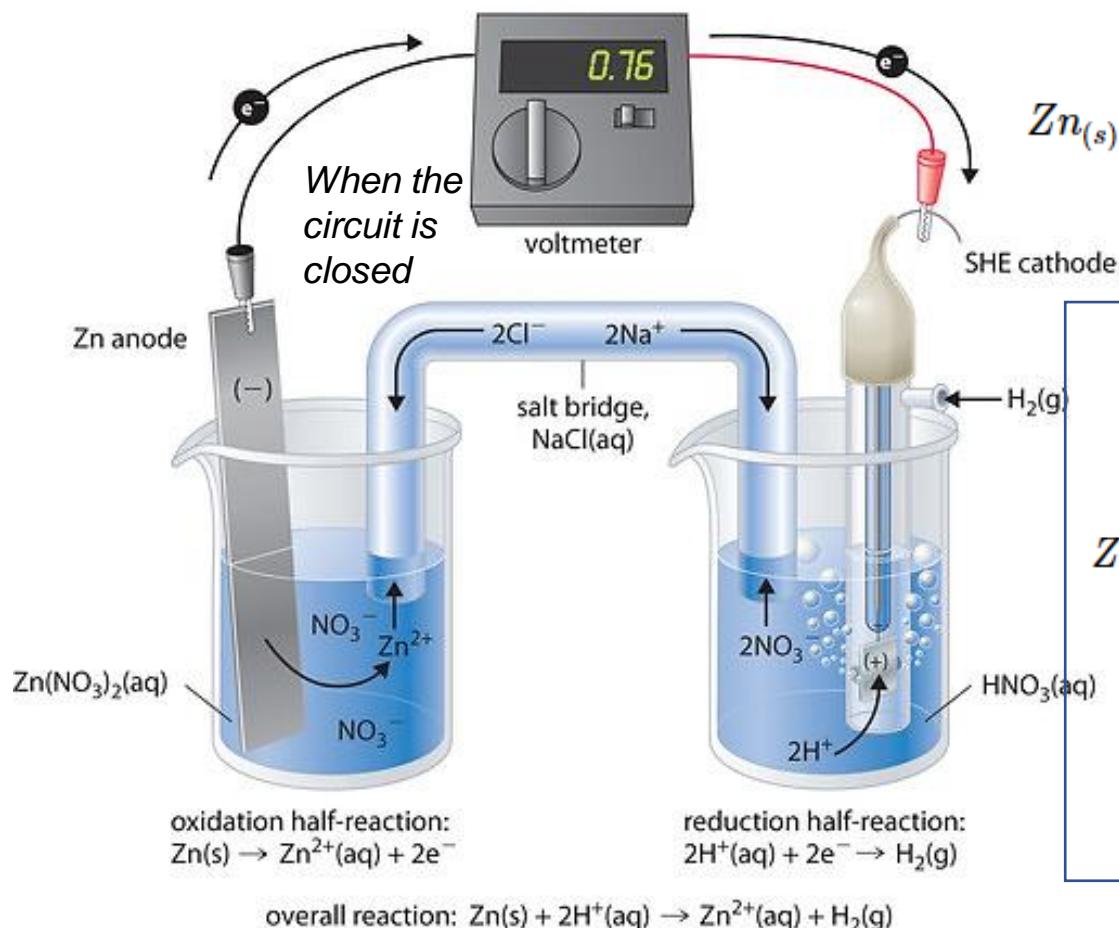
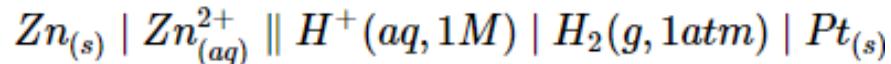
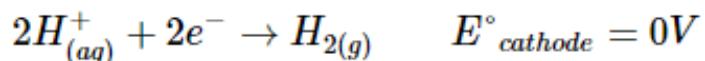


Diagram for this galvanic cell



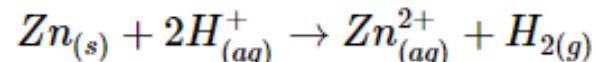
Cathode:



Anode:



Overall



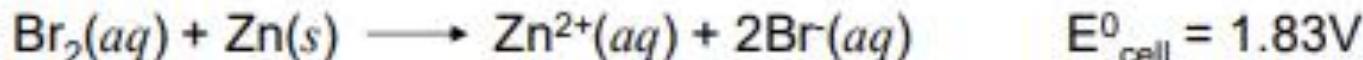
$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.76 V$$

We can use this procedure described to measure the standard potentials for a wide variety of chemical substances

Calculating an unknown $E^{\circ}_{\text{half-cell}}$ from E°_{cell}

Sample Problem

PROBLEM: A voltaic cell houses the reaction between aqueous bromine and zinc metal:



Calculate $E^{\circ}_{\text{bromine}}$ given $E^{\circ}_{\text{zinc}} = -0.76\text{V}$

PLAN: The reaction is spontaneous as written since the E°_{cell} is (+). Zinc is being oxidized and is the anode. Therefore the $E^{\circ}_{\text{bromine}}$ can be found using $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$.

SOLUTION: anode: $\text{Zn}(\text{s}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \quad E = +0.76$

E°_{Zn} as $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Zn}(\text{s})$ is -0.76V

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 1.83 = E^{\circ}_{\text{bromine}} - (-0.76)$$

$$E^{\circ}_{\text{bromine}} = 1.83 + 0.76 = 1.07\text{V}$$

Electrochemical Series

- 👉 Created by comparing different electrode potentials to conventional **SHE**, it helps in the arrangement of electrodes.
- 👉 It describes the arrangement of electrode in order of their increasing potential values.

Features:

- All reduction potentials are given on hydrogen scale.
- When an electrode has a greater potential, it is easier to reduce it.
- Oxidation is easier for electrode with low potential.
- A high (+ve) electrode potential is placed at the top of the EMF series. In contrast, those with a lower (-ve) electrode potentials are placed at the bottom.

Electrochemical Series



Uses:

Comparison of the oxidizing & reducing strengths.

Comparison of reactivities of the metals.

Calculation of the EMF of electrochemical cell.

Predicting the feasibility of redox reaction.

Electrochemical Series

1

Comparison of the relative oxidizing & reducing strengths

	Half Reaction	Standard Potential (V)
F_2	$+ 2e^- \rightleftharpoons 2F^-$	+2.87
Pb^{4+}	$+ 2e^- \rightleftharpoons Pb^{2+}$	+1.67
Cl_2	$+ 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$		+1.23
Ag^+	$+ 1e^- \rightleftharpoons Ag$	+0.80
Fe^{3+}	$+ 1e^- \rightleftharpoons Fe^{2+}$	+0.77
Cu^{2+}	$+ 2e^- \rightleftharpoons Cu$	+0.34
$2H^+$	$+ 2e^- \rightleftharpoons H_2$	0.00
Pb^{2+}	$+ 2e^- \rightleftharpoons Pb$	-0.13
Fe^{2+}	$+ 2e^- \rightleftharpoons Fe$	-0.44
Zn^{2+}	$+ 2e^- \rightleftharpoons Zn$	-0.76
Al^{3+}	$+ 3e^- \rightleftharpoons Al$	-1.66
Mg^{2+}	$+ 2e^- \rightleftharpoons Mg$	-2.36
Li^+	$+ 1e^- \rightleftharpoons Li$	-3.05

examples

Zn (-0.76 V)	Au (+1.50 V)	Zn (-0.76 V)	Cu (+0.34 V)
Anode	Cathode	Anode	Cathode
Ni (-0.25 V)	Ag (+0.80 V)	Al (-1.66 V)	Cu (+0.34 V)
Anode	Cathode	Anode	Cathode

Electrochemical Series1

2

Comparison of reactivities of the metals.

- An electrode with a positive value has a higher reduction potential. Hence, it works strong **oxidizing agent (SOA)**.
- An electrode with a negative value has a higher oxidation potential. Hence, it works strong **Reducing agent (SRA)**.

Half Reaction	Standard Potential (V)
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.67
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Ag^+ + 1e^- \rightleftharpoons Ag$	+0.80
$Fe^{3+} + 1e^- \rightleftharpoons Fe^{2+}$	+0.77
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.13
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.66
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.36
$Li^+ + 1e^- \rightleftharpoons Li$	-3.05

examples

Zn (-0.76 V)	Cu (+0.34 V)
SRA	SOA

Ni (-0.25 V)	Ag (+0.80 V)
SRA	SOA

Zn (-0.76 V)	Au (+1.50 V)
SRA	SOA

Electrochemical Series1



Calculation of the EMF of electro-chemical cell.

The emf associated with any redox reaction can be calculated.

$$E_{cell}^o = E_{cathode \text{ (reduction)}}^o - E_{anode \text{ (oxidation)}}^o$$

Adding EMF

For Eg:

- For a reaction, $2\text{Ag}^+ \text{ (aq)} + \text{Cd} \rightarrow 2\text{Ag}^+ \text{ Cd}^{+2}\text{(aq)}$
- The SRP of $\text{Ag}^+/\text{Ag} = 0.80 \text{ V}$, $\text{Cd}^{+2}/\text{Cd} = -0.40 \text{ V}$
- Using the formula,
- $E_{cell}^o = 0.80 - (-0.40)$
- $E_{cell}^o = 1.20 \text{ V}$

Electrochemical Series1



To predict the spontaneity of redox reaction

Any redox reaction would occur spontaneously if the free energy change (ΔG) is negative.

$$E_{cell}^o = E_{cathode \ (reduction)}^o - E_{anode \ (oxidation)}^o$$

ΔG° ; is negative	Spontaneous reaction
ΔG° ; is positive	Non-spontaneous reaction

- Spontaneous redox reaction
 - positive E° (standard conditions)
 - positive E (non-standard conditions)
 - negative ΔG
- Non-spontaneous redox reactions:
 - negative E°
 - negative E
 - positive ΔG

Standard Electrode Potentials (electrochemical series)

	Reduction Half-Reaction	E° (V)	
Stronger oxidizing agent			
	$\text{F}_2(g) + 2 \text{e}^- \longrightarrow 2 \text{F}(aq)$	2.87	
	$\text{H}_2\text{O}_2(aq) + 2 \text{H}^+(aq) + 2 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(l)$	1.78	
	$\text{MnO}_4^-(aq) + 8 \text{H}^+(aq) + 5 \text{e}^- \longrightarrow \text{Mn}^{2+}(aq) + 4 \text{H}_2\text{O}(l)$	1.51	
	$\text{Cl}_2(g) + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-(aq)$	1.36	
	$\text{Cr}_2\text{O}_7^{2-}(aq) + 14 \text{H}^+(aq) + 6 \text{e}^- \longrightarrow 2 \text{Cr}^{3+}(aq) + 7 \text{H}_2\text{O}(l)$	1.33	
	$\text{O}_2(g) + 4 \text{H}^+(aq) + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(l)$	1.23	
	$\text{Br}_2(l) + 2 \text{e}^- \longrightarrow 2 \text{Br}^-(aq)$	1.09	
	$\text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)$	0.80	
	$\text{Fe}^{3+}(aq) + \text{e}^- \longrightarrow \text{Fe}^{2+}(aq)$	0.77	
	$\text{O}_2(g) + 2 \text{H}^+(aq) + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2(aq)$	0.70	
	$\text{I}_2(s) + 2 \text{e}^- \longrightarrow 2 \text{I}^-(aq)$	0.54	
	$\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(aq)$	0.40	
	$\text{Cu}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Cu}(s)$	0.34	
	$\text{Sn}^{4+}(aq) + 2 \text{e}^- \longrightarrow \text{Sn}^{2+}(aq)$	0.15	
	$2 \text{H}^+(aq) + 2 \text{e}^- \longrightarrow \text{H}_2(g)$	0	
	$\text{Pb}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Pb}(s)$	-0.13	
	$\text{Ni}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Ni}(s)$	-0.26	
	$\text{Cd}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Cd}(s)$	-0.40	
	$\text{Fe}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Fe}(s)$	-0.45	
	$\text{Zn}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Zn}(s)$	-0.76	
	$2 \text{H}_2\text{O}(l) + 2 \text{e}^- \longrightarrow \text{H}_2(g) + 2 \text{OH}^-(aq)$	-0.83	
	$\text{Al}^{3+}(aq) + 3 \text{e}^- \longrightarrow \text{Al}(s)$	-1.66	
	$\text{Mg}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Mg}(s)$	-2.37	
	$\text{Na}^+(aq) + \text{e}^- \longrightarrow \text{Na}(s)$	-2.71	
	$\text{Li}^+(aq) + \text{e}^- \longrightarrow \text{Li}(s)$	-3.04	
Weaker oxidizing agent			Stronger reducing agent

These data allow us to compare the oxidative and reductive strengths of a variety of substances.

Element	Electrode Reaction (Reduction)	Standard Electrode Reduction Potential E° , Volt
Li	$\text{Li}^+ + \text{e}^- = \text{Li}$	-3.05
K	$\text{K}^+ + \text{e}^- = \text{K}$	-2.925
Ca	$\text{Ca}^{2+} + 2\text{e}^- = \text{Ca}$	-2.87
Na	$\text{Na}^+ + \text{e}^- = \text{Na}$	-2.714
Mg	$\text{Mg}^{2+} + 2\text{e}^- = \text{Mg}$	-2.37
Al	$\text{Al}^{3+} + 3\text{e}^- = \text{Al}$	-1.66
Zn	$\text{Zn}^{2+} + 2\text{e}^- = \text{Zn}$	-0.7628
Cr	$\text{Cr}^{3+} + 3\text{e}^- = \text{Cr}$	-0.74
Fe	$\text{Fe}^{2+} + 2\text{e}^- = \text{Fe}$	-0.44
Cd	$\text{Cd}^{2+} + 2\text{e}^- = \text{Cd}$	-0.403
Ni	$\text{Ni}^{2+} + 2\text{e}^- = \text{Ni}$	-0.25
Sn	$\text{Sn}^{2+} + 2\text{e}^- = \text{Sn}$	-0.14
Pb	$\text{Pb}^{2+} + 2\text{e}^- = \text{Pb}$	-0.13
H ₂	$2\text{H}^+ + 2\text{e}^- = \text{H}_2$	0.00
Cu	$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$	+0.337
I ₂	$\text{I}_2 + 2\text{e}^- = 2\text{I}^-$	+0.535
Ag	$\text{Ag}^+ + \text{e}^- = \text{Ag}$	+0.80
Hg	$\text{Hg}^{2+} + 2\text{e}^- = \text{Hg}$	+0.885
Br ₂	$\text{Br}_2 + 2\text{e}^- = 2\text{Br}^-$	+1.08
Cl ₂	$\text{Cl}_2 + 2\text{e}^- = 2\text{Cl}^-$	+1.36
Au	$\text{Au}^{3+} + 3\text{e}^- = \text{Au}$	+1.50
F ₂	$\text{F}_2 + 2\text{e}^- = 2\text{F}^-$	+2.87

Sample Problem Describing a Voltaic Cell with Diagram and Notation

PROBLEM:

Draw a diagram, show balanced equations, and write the notation for a voltaic cell that consists of one half-cell with a Cr bar in a $\text{Cr}(\text{NO}_3)_3$ solution, another half-cell with an Ag bar in an AgNO_3 solution, and a KNO_3 salt bridge. Measurement indicates that the Cr electrode is negative relative to the Ag electrode.

PLAN:

- ✓ From the given contents of the half-cells, we **write the half-reactions**.
- ✓ To **determine** which is the **anode compartment** (oxidation) and which is the cathode (reduction), we note the **relative electrode charges**.
- ✓ Electrons are released into the anode during oxidation, so it has a negative charge. Since Cr is negative, it must be the anode, and Ag is the cathode.

Sample Problem

SOLUTION:

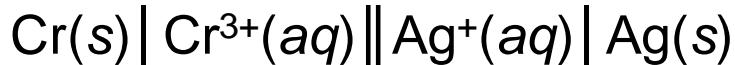
The half-reactions are:



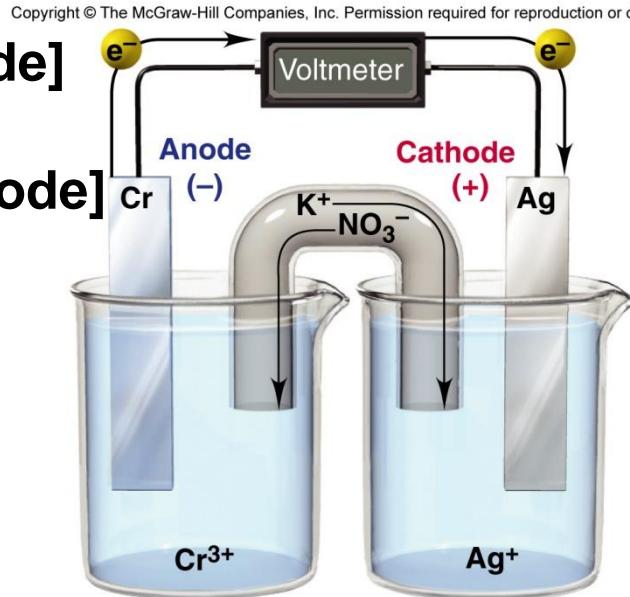
The balanced overall equation is:



The cell notation is given by:



The cell diagram shows the anode on the left and the cathode on the right.



Reference electrodes

Are those whose half-cell potentials are known, constant, and totally insensitive to the composition of solutions.

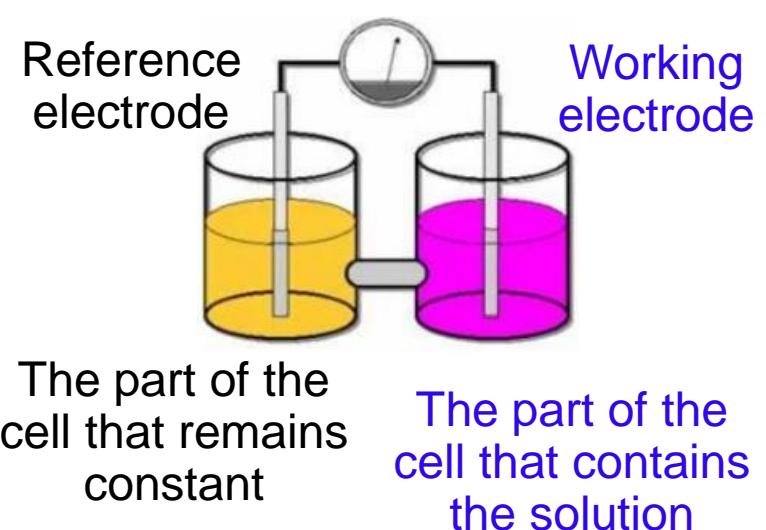
It can serve as both the anode and the cathode.

It can be used as a half-cell to construct of an electrochemical cell.

In conjunction with this reference is the indicator/working.

Desirable characters

- It should be easy to construct.
- It should develop potentials.



Application of Reference Electrodes

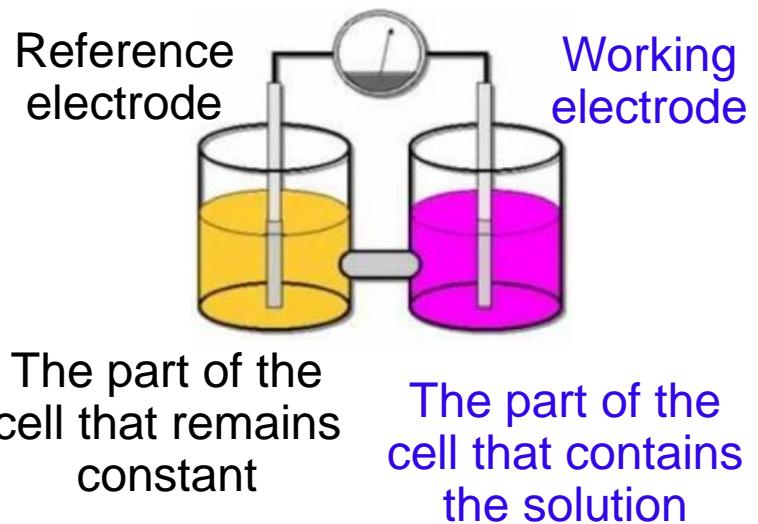
It can be used to determine a range of pH values of solutions.



Another electrode potential can be easily calculated.



It is used to measure pH & electrical potential of the solution.



Reference Electrodes

Types of reference electrodes

Primary reference electrode

Secondary reference electrode

SHE is called a primary reference electrode.

The electrode whose potential is determined by connecting to the SHE

SHE = Standard hydrogen electrode

Exs:
Calomel & Ag/AgCl electrodes

Construction & working of SHE



It used to determine the electrode potential of a cell.

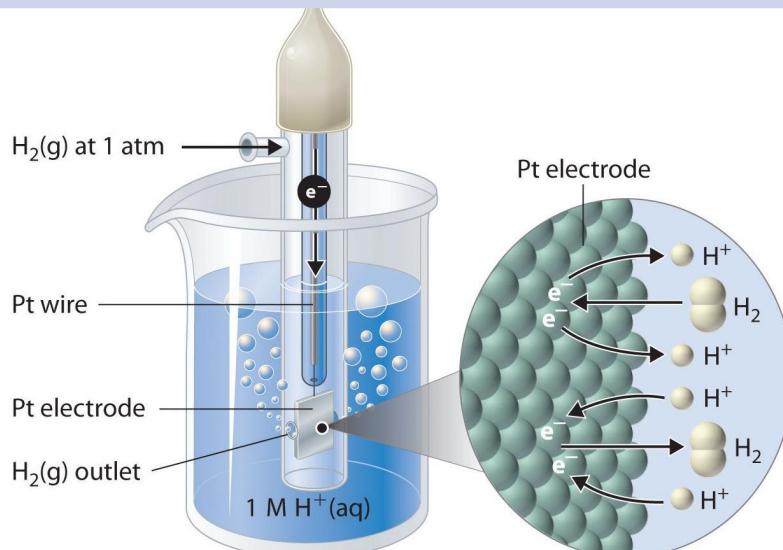
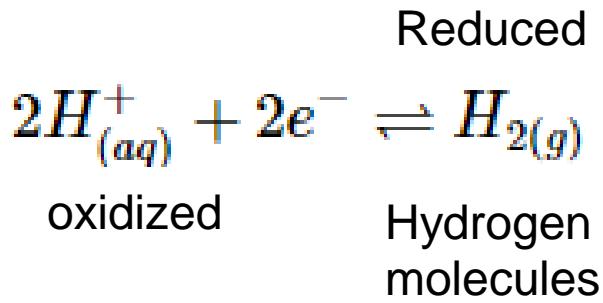


It can work both as an anode and as a cathode



SHE has the advantage of not consuming the Pt metal electrode.

Pr



half-reaction at Pt surface:
 $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$

Limitation of SHE

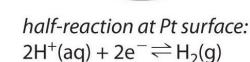
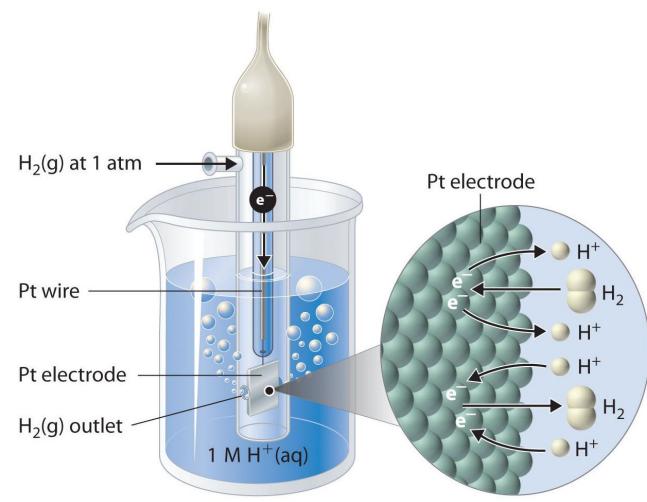
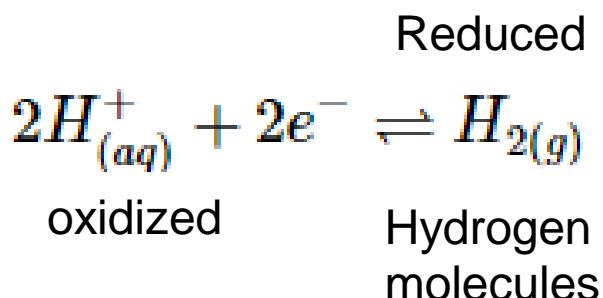
It is difficult to construct SHE.

Keeping the concentration of H⁺ at 1M is extremely difficult

To keep H₂ gas at 1 atm during all determination is difficult.

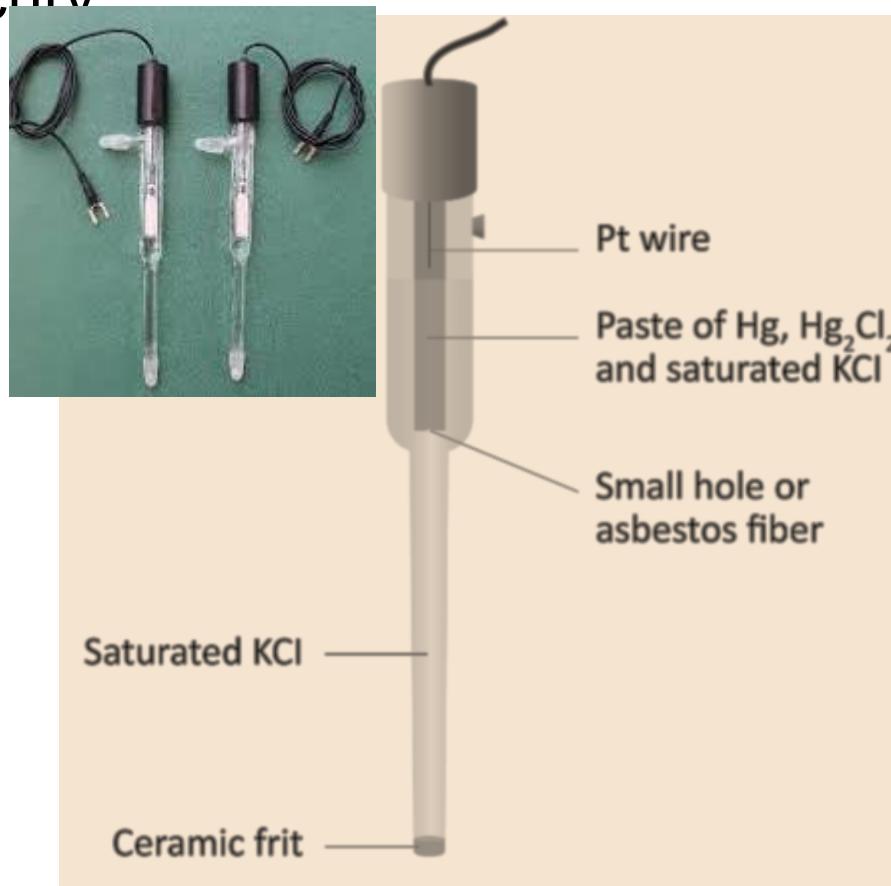
A platinum electrode is poisoned by gas impurities

Oxidizing agents cannot be used with it.



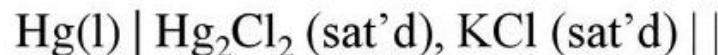
Construction calomoel electrode; SCE

- 👉 Its potential remains constant over a long time, making it the most common secondary electrode.
 - 👉 Is based on reactions between mercury (I) chloride (calomel) and elemental mercury
-
- ✓ Frit permits electrical contact with a solution outside the electrode.
 - ✓ Glass wool for electrical contact b/w the contents of both tubes.
 - ✓ Mercury paste is packed on the innermost tube, with calomel being dispersed in a Sat. KCl.
 - ✓ aq. KCl, acts as a salt bridge b/w the interior cell and the exterior solution.



Working of calomoel electrode; SCE

Cell shorthand for SCE is



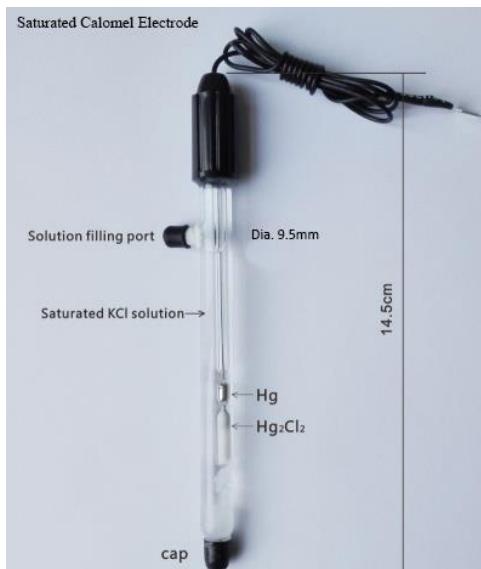
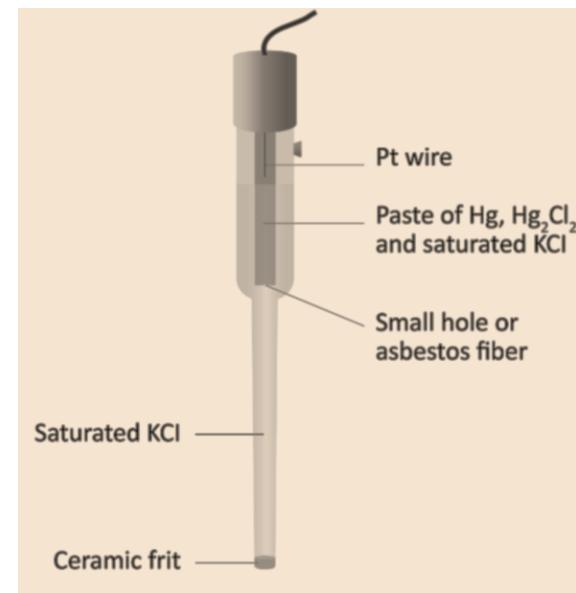
It can act as anode or cathode depending on the nature of the other electrode.

electrode reaction in calomel hal-cell



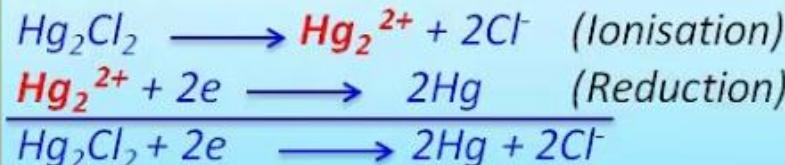
$$E^\circ = + 0.268\text{V}$$

$$E = E^\circ - (0.05916/2) \log[\text{Cl}^-]^2 = 0.244 \text{ V}$$

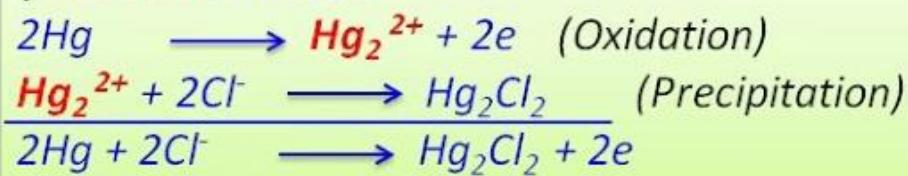


Working of the Electrode:

If it acts as Cathode:



If it acts as Anode:

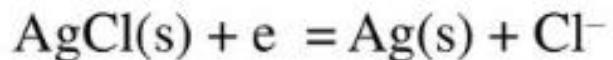
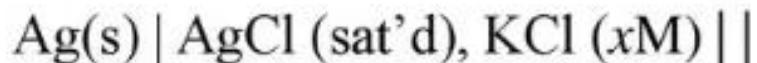


Construction silver/silver chloride electrode

Widely used because simple, inexpensive, very stable non-toxic.

Is more compact, better & faster.

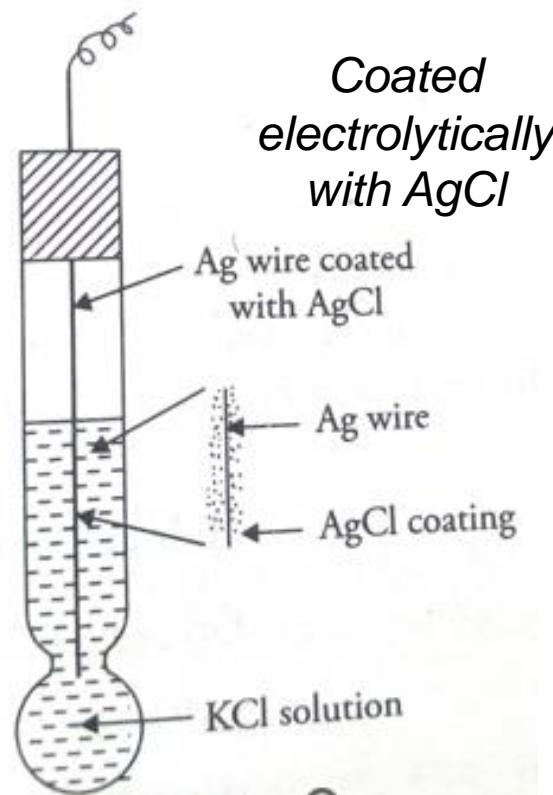
Evaporation does not change the saturated nature of the solution/potential.



$$E^\circ = +0.244\text{V}$$

$$E = E^\circ - (0.05916/1) \log [\text{Cl}^-]$$

$$E \text{ (saturated KCl)} = + 0.199\text{V (25}^\circ\text{C)}$$



silver/silver chloride electrode

Advantages

- 👉 It is more difficult to prepare than SCE;
- 👉 AgCl in the electrode has large solubility in sat. KCl.



Disadvantages

- 👉 It has better thermal stability
- 👉 Less toxicity & environmental problems with consequent cleanup & disposal difficulties.

Glass electrode It is the most useful and versatile of all electrodes used for pH measurements. It is based on the principle that when two solutions of different hydrogen ion concentrations are separated by a glass membrane, a potential difference develops across the glass membrane. The magnitude of the potential difference depends upon the difference in the concentration of the hydrogen ions in the two solutions. The glass membrane is a special type of membrane having the approximate composition of 72 % SiO_2 , 22 % Na_2O and 6 % CaO .

A glass electrode consists of a thin walled bulb of pH sensitive glass sealed to a stem of non-pH sensitive high resistance glass (Fig. 14.13). Inside the glass electrode is a silver-silver chloride electrode or calomel electrode or simply a Pt wire dipped in 0.1 N HCl solution.

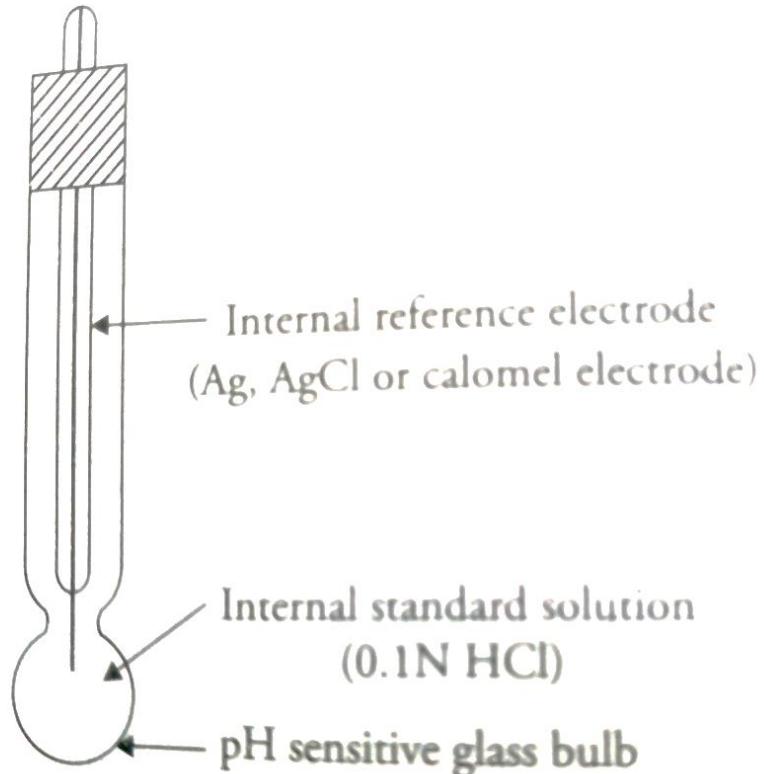
This glass electrode is dipped in a solution of varying hydrogen ion concentration (unknown pH) and is connected to an external reference electrode, usually a calomel electrode, with the help of a salt bridge.

The cell may be represented as

$\text{Ag}, \text{AgCl}, 0.1\text{N HCl} / \text{Glass} / \text{Experimental solution} / \text{KCl}, \text{Hg}_2\text{Cl}_2(\text{s}), \text{Hg}$

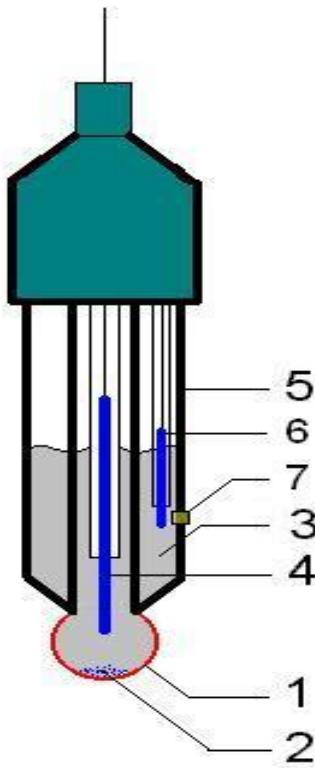
or

$\text{Pt}, 0.1\text{N HCl} / \text{Glass} / \text{Experimental solution} / \text{KCl}, \text{Hg}_2\text{Cl}_2(\text{s}), \text{Hg}$



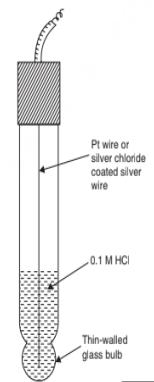
Ion Selective Electrode.

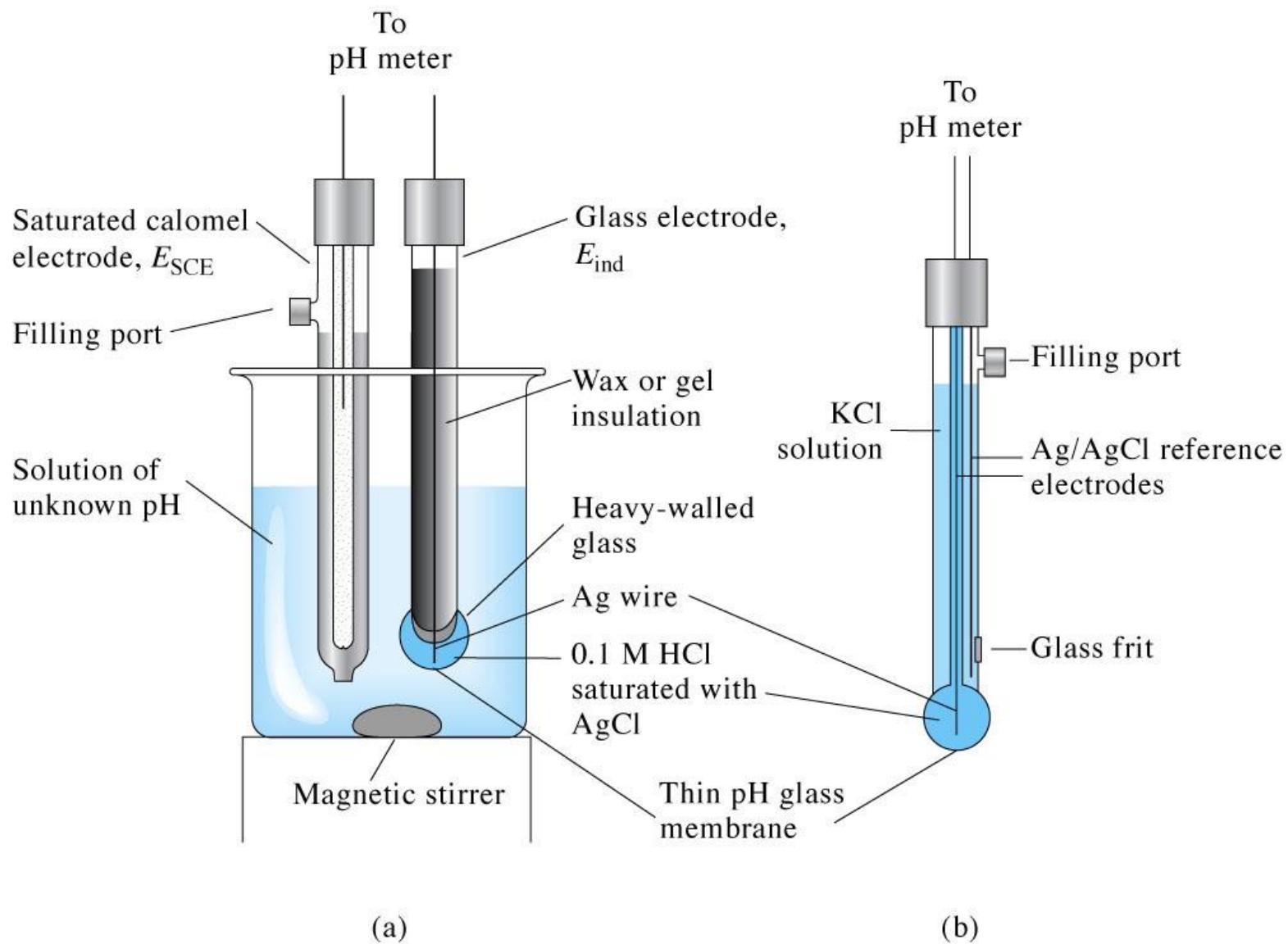
- ❖ It is sensitive to a specific ion present in an electrolyte.
- ❖ The potential of this depends upon the activity of this ion in the electrolyte.
- ❖ Magnitude of potential of this electrode is an indicator of the activity of the specific ion in the electrolyte.
- ❖ *This type of electrode is called indicator electrode.

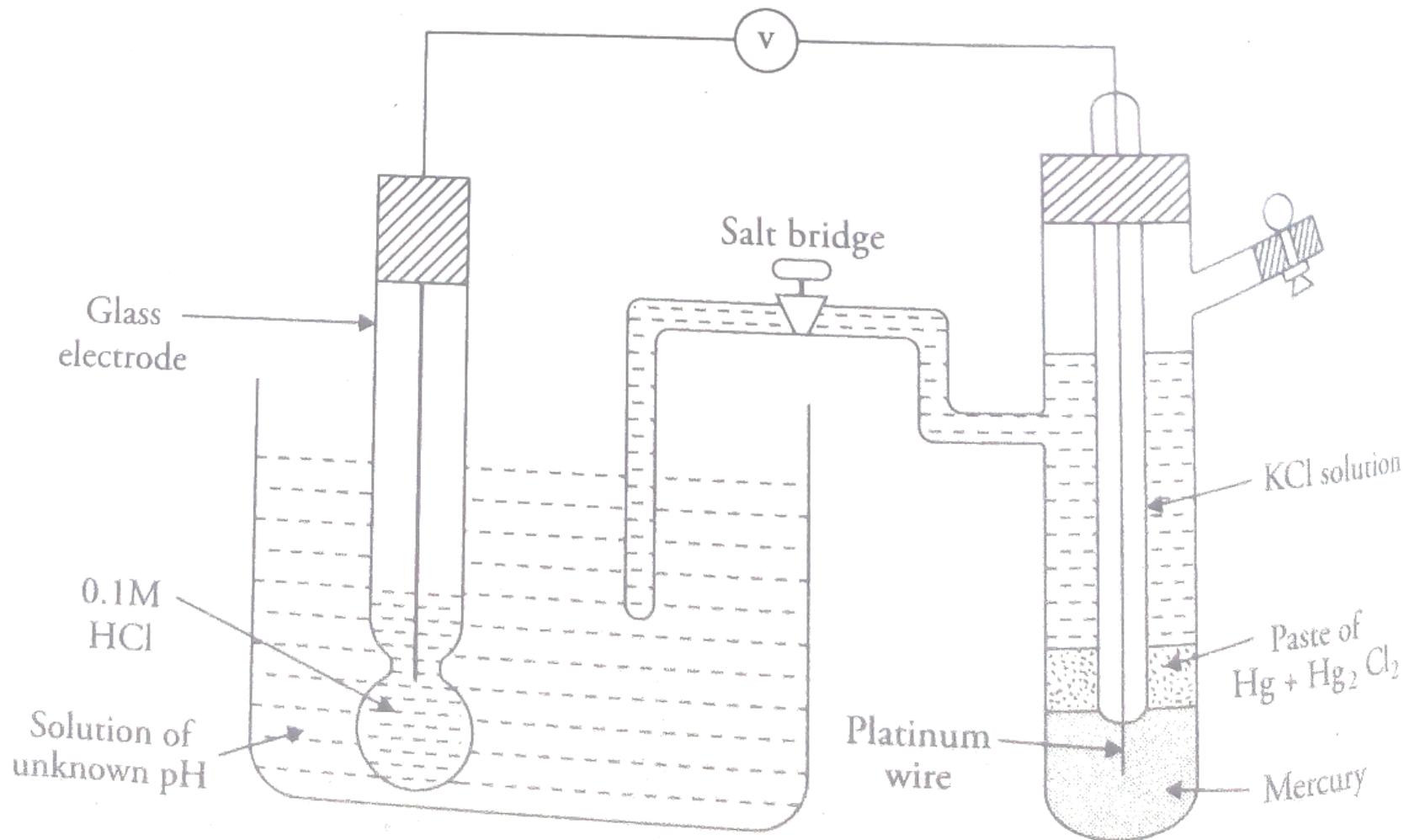


Scheme of typical pH glass electrode

1. a sensing part of electrode,
2. a bulb made from a specific glass sometimes electrode contain small amount of AgCl precipitate inside the glass electrode
- 3 internal solution, usually 0.1M HCl for pH electrodes
4. internal electrode, usually silver chloride electrode or calomel electrode
5. body of electrode, made from non-conductive glass or plastics.
6. reference electrode, usually the same type as 4
7. junction with studied solution, usually made from ceramics or capillary with asbestos or quartz fiber.







$\text{Ag} / \text{AgCl}(s), \text{HCl (0.1M)} / \text{glass}$

$$E_{\text{glass}} = E_{\text{glass}}^0 - \frac{2.303RT}{nF} \log \frac{[\text{H}_2]^{1/2}}{[\text{H}^+]}$$

$$E_{\text{glass}} = E_{\text{glass}}^0 - 0.0591 \log \frac{1}{[\text{H}^+]}$$

$$E_{\text{glass}} = E_{\text{glass}}^0 - 0.0591 \text{ pH}$$

To find pH, this is coupled with a calomel electrode (Fig 14.16). The cell is formed
 $\text{Ag} / \text{AgCl (s)} / \text{HCl (0.1M)} / \text{glass} // \text{Solution of unknown pH} / \text{Calomel electrode}$
(The electrode potentials are expressed as reduction potentials)

$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{glass}}$$

$$E_{\text{cell}} = E_{\text{calomel}} - (E_{\text{glass}}^0 - 0.0591 \text{ pH})$$

$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{glass}}^0 + 0.0591 \text{ pH}$$

$$\text{pH} = \frac{E_{\text{cell}} - E_{\text{calomel}} + E_{\text{glass}}^0}{0.0591}$$

Thermodynamics of cell reactions

Free energy & Electrical work

Free energy and potential in electrochemical cells are related in the following way:

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

n = mol of e^- transferred

F is the Faraday constant = 9.65×10^4 J/V·mol

Cell potential (E°_{cell})

When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} is as follows:

$$\Delta G^\circ = -nFE_{cell}^\circ$$

Spontaneous redox reaction;

Positive E°

Negative; ΔG

Non-Spontaneous redox reaction;

Negative E°

Positive ΔG

Free energy & Electrical work

The following equation relates the standard free-energy change to the equilibrium constant:

$$\Delta^\circ = -RT \ln k$$

Based on the relationship between the standard free-energy change and the standard cell potential, we can write

$$-nFE_{cell}^\circ = -RT \ln k$$

By rearranging this equation, $E_{cell}^\circ = \frac{RT}{nF} \ln k$

For T=298K, the equation can be simplified as follows:,

$$E_{cell}^\circ = \frac{0.0592 V}{n} \log k$$

Nernst equation

Following the connection between free energy and cell potentials, non-standard concentrations follow. Recall that

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Where Q is the reaction quotient

Converting to cell potentials:

$$-nFE_{cell} = -nFE_{cell}^\circ + RT \ln Q$$

or

$$E_{cell} = E_{cell}^\circ - \frac{RT}{nF} \ln Q$$

It is a generalized Nernst equation that can be applied to any temperature.

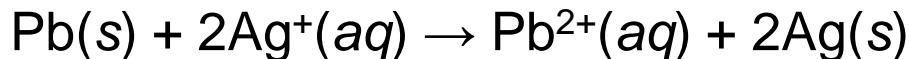
Rewriting it as follows simplifies it for reactions occurring at 25 °C (298.15 K)

$$E_{cell} = E_{cell}^\circ - \frac{0.0592 V}{n} \log k$$

Sample Problem

Calculating K and ΔG° from E°_{cell}

PROBLEM: Lead can displace silver from solution, and silver occurs in trace amounts in some ores of lead.



Therefore, silver is a valuable byproduct in the industrial extraction of lead from its ore. Calculate K and ΔG° at 298.15 K for this reaction.

PLAN: ✓ We divide the spontaneous redox reaction into the half-reactions.
✓ Use values from Appendix D to calculate E°_{cell} .
✓ From this we can find K and ΔG° .

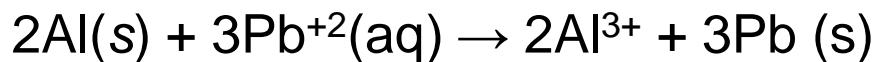
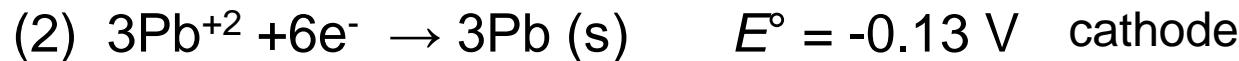
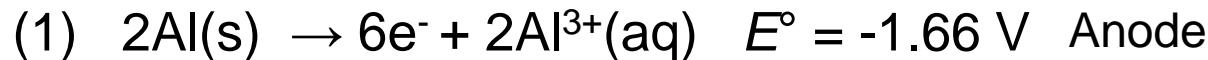
SOLUTION:

Writing the half-reactions with their E° values:

- (1) $\text{Ag}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{Ag(s)} \quad E^\circ = 0.80 \text{ V}$
- (2) $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb(s)} \quad E^\circ = -0.13 \text{ V}$

Sample Problem Solution

We need to reverse equation (2) and multiply equation (1) by 2:



$$E^\circ_{\text{cell}} = -0.13 - (-1.66) = 1.53 \text{ V}$$

$$E^\circ_{\text{cell}} = \frac{0.0592 \text{ V}}{6} \log K$$

$$\log K = \frac{1.53 \text{ V} \times 6}{0.0592 \text{ V}} = 154.80 \quad K = 10^{154.8}$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -\frac{6 \text{ mol e}^-}{\text{mol}_{\text{rxn}}} \times \frac{96.5 \text{ kJ}}{\text{V} \cdot \text{mol e}^-} \times 1.53 \text{ V}$$

$$= -8.8 \times 10^2 \text{ kJ/mol}_{\text{rxn}}$$

Sample Problem

Calculating the Potential of a Concentration Cell

PROBLEM: A concentration cell consists of two Ag/Ag⁺ half-cells. In half-cell A, the electrolyte is 0.0100 M AgNO₃; in half-cell B, it is 4.0x10⁻⁴ M AgNO₃. What is the cell potential at 298.15 K?

Nernst Equation

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q$$

- When $Q < 1$, [reactant] > [product], $\ln Q < 0$, so $E_{\text{cell}} > E^{\circ}_{\text{cell}}$
- When $Q = 1$, [reactant] = [product], $\ln Q = 0$, so $E_{\text{cell}} = E^{\circ}_{\text{cell}}$
- When $Q > 1$, [reactant] < [product], $\ln Q > 0$, so $E_{\text{cell}} < E^{\circ}_{\text{cell}}$

We can simplify the equation as before for $T = 298.15$ K:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592 \text{ V}}{n} \log Q$$

Sample Problem

Calculating the Potential of a Concentration Cell

PROBLEM: A concentration cell consists of two Ag/Ag⁺ half-cells. In half-cell A, the electrolyte is 0.0100 M AgNO₃; in half-cell B, it is 4.0x10⁻⁴ M AgNO₃. What is the cell potential at 298.15 K?

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We can simplify the equation as before for $T = 298.15$ K:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592 \text{ V}}{n} \log Q$$

Electrochemical Processes in Batteries

A *battery* consists of self-contained voltaic cells arranged in series, so their individual voltages are added.

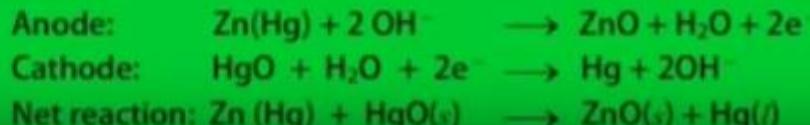
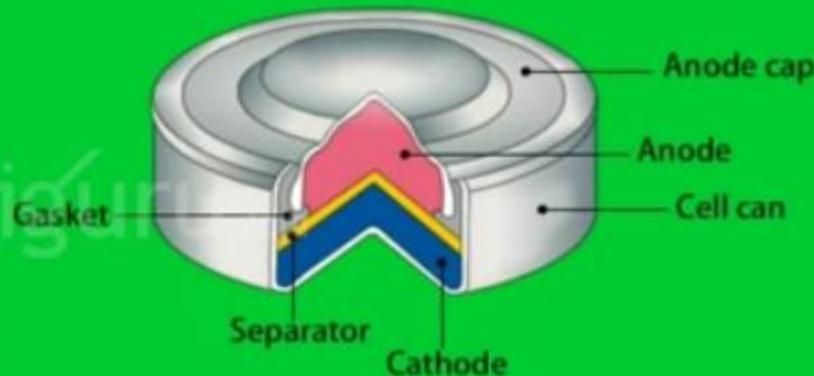
A *primary* battery cannot be recharged. The battery is “dead” when the cell reaction has reached equilibrium.

A *secondary* battery is rechargeable. Once it has run down, electrical energy is supplied to reverse the cell reaction and form more reactant.

Mercury Cell

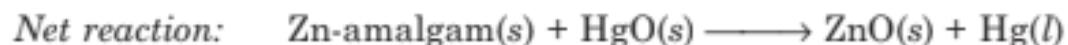
- In mercury cell zinc-mercury amalgam is the anode and a paste of HgO and carbon acts as cathode. The electrolyte is a paste of KOH and ZnO .

Mercury Cell



Mercury Battery

This type of battery is constructed of zinc-amalgam (a solution of Zn in mercury) as anode and a paste of KOH, Zn(OH)_2 and HgO as cathode. The anode and the cathode are divided by a paper. The paper permits the migration of ions. The cell reaction is:

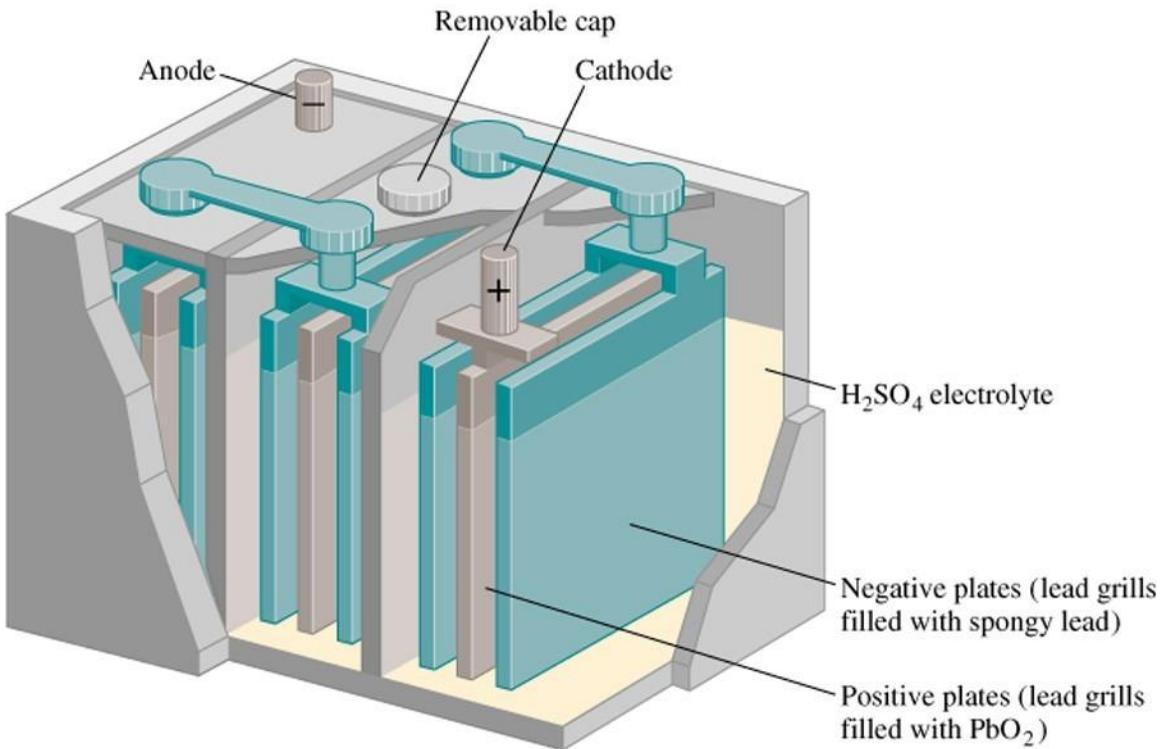


The entire cell is covered in a stainless steel case. The size is small. It is expensive.

Use: It finds its use in pacemakers, hearing aids, digital watches etc.

Batteries

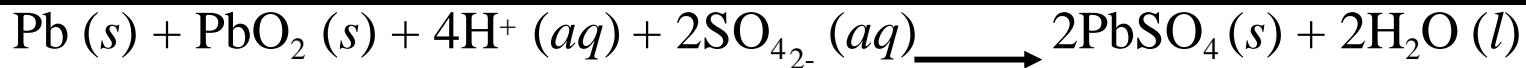
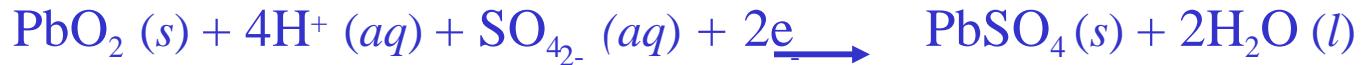
Lead storage
battery



Anode:

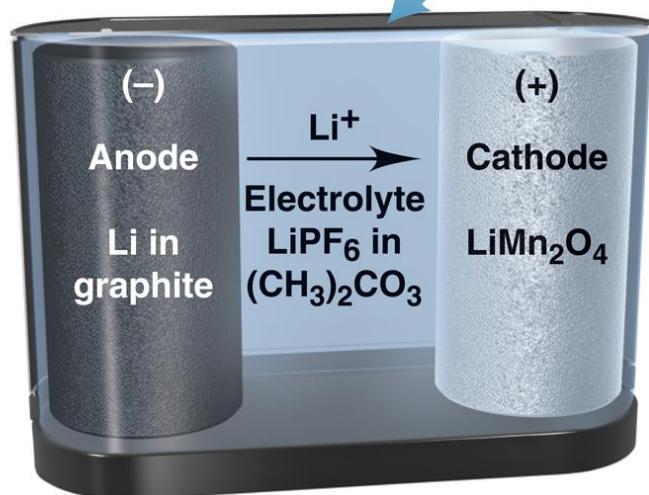
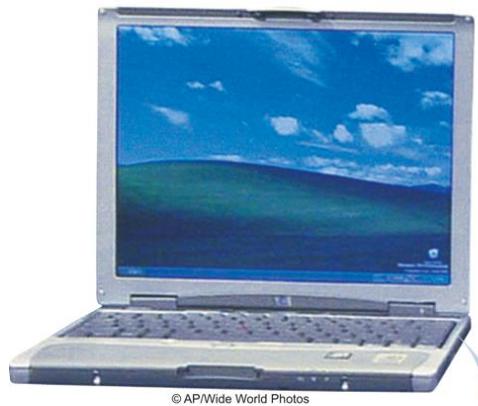


Cathode:



Lithium-ion battery.

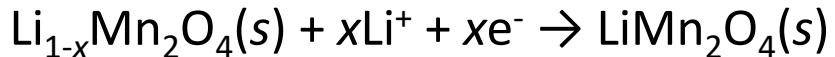
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Anode (oxidation):



Cathode (reduction):



Overall (cell) reaction:

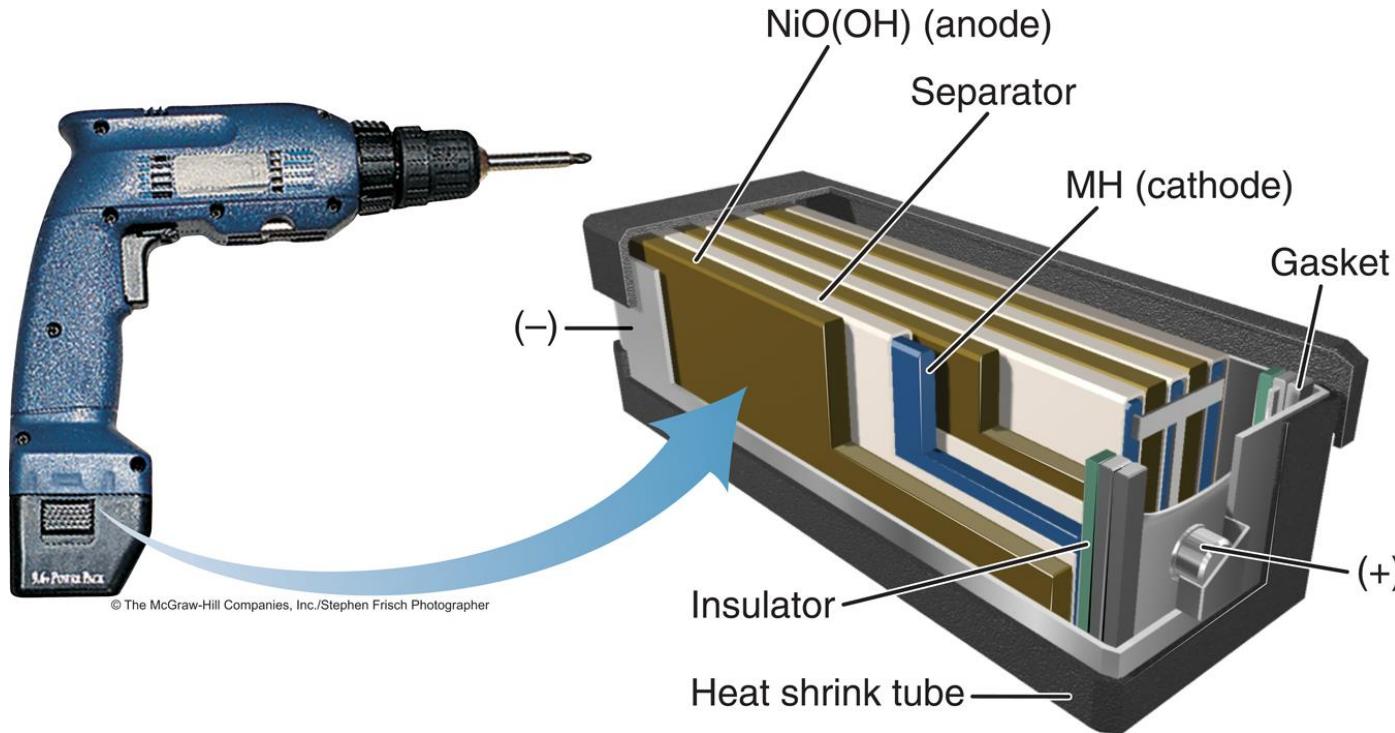


$$E_{\text{cell}} = 3.7 \text{ V}$$

The secondary (rechargeable) lithium-ion battery is used to power laptop computers, cell phones, and camcorders.

Nickel-metal hydride battery

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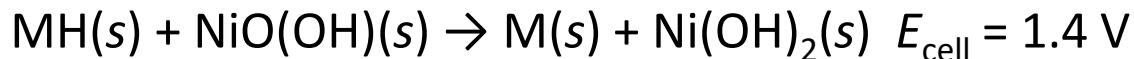


Anode (oxidation):



Cathode (reduction): $\text{NiO(OH)}(s) + \text{H}_2\text{O}(l) + \text{e}^- \rightarrow \text{Ni(OH)}_2(s) + \text{OH}^-(aq)$

Overall (cell) reaction:



Fuel Cell vs. Battery

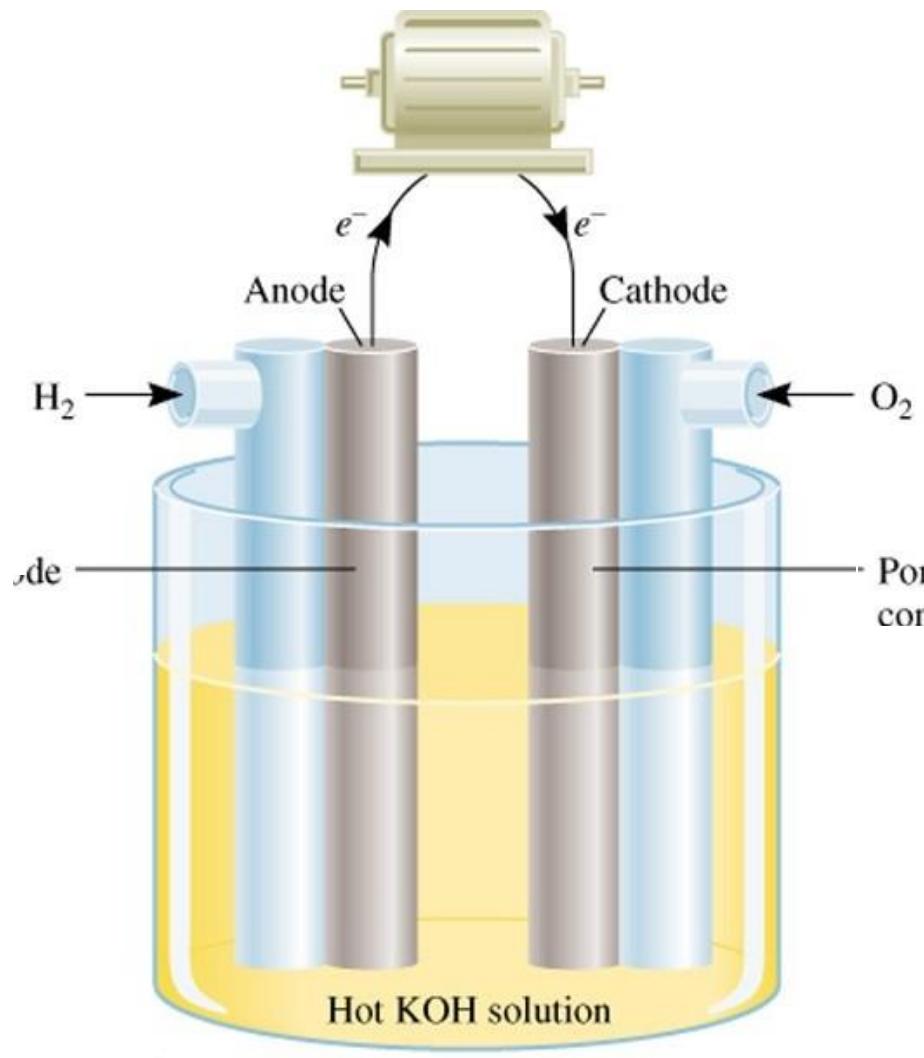
- Battery; Energy storage device
 - Reactant chemicals already in device
 - Once Chemicals used up; discard (unless rechargeable)
- Fuel Cell; Energy conversion device
 - Won't work unless reactants supplied
 - Reactants continuously supplied; products continuously removed

Fuel Cells

In a *fuel cell*, also called a *flow cell*, reactants enter the cell and products leave, generating electricity through controlled combustion.

Reaction rates are lower in fuel cells than in other batteries, so an *electrocatalyst* is used to decrease the activation energy.

Fuel Cell



A ***fuel cell*** is an electrochemical cell that requires a continuous supply of reactants to keep functioning





**Thanks You
For Your Attention**

Do u have
**Any
QUESTION?**

CONCENTRATION CELL

- It is a galvanic cell in which electrical energy is produced by the transfer of substance from one electrode having higher concentrated solution to other electrode having lower concentrated solution.
- It is made up of two half cells having identical electrodes, identical electrolyte with change in concentrations.
- The two half cells are joined by a salt bridge or a semi permeable membrane.
- Concentration cells are of two types:
 - Concentration cell without transfer
 - Concentration cell with transfer

CONCENTRATION CELL

- Concentration cell without transfer
 - When two hydrogen electrodes of different gas pressures P_1 and P_2 ($P_1 > P_2$) are immersed in the same solution of hydrogen ions, oxidation of hydrogen takes place at left hand electrode and reduction of hydrogen takes place at right hand electrode.
 - Cell representation: Pt, $H_2 (P_1) : H^+ \parallel H^+ : H_2 (P_2)$, Pt

Electrode reactions:



- From the above, there is no overall chemical change and there is only a transfer of hydrogen gas from the electrode with pressure P_1 , to the electrode with pressure P_2 .
- In this case, the emf of electrode depends only on the two pressures and is independent of the concentration of hydrogen ions in which electrodes are immersed.

$$E_{cell} = \frac{2.303RT}{2F} \log \frac{P_1}{P_2}$$

$$E_{cell} = \frac{0.059}{2} \log \frac{P_1}{P_2}$$

Concentration cell with transfer

- In this, electrodes are identical but electrolyte solution has different concentrations.
- Due to difference in the concentration of electrolyte there occurs corresponding change in the potential of the electrodes dipping in them.
- When the two electrodes of same metal (M) are dipped in of its own ion solution with different concentrations of C_1 and C_2 ($C_2 > C_1$) and connected with a salt bridge, the following reactions takes place:



➤ Cell representation: $M : M^{+n} (C_1) \parallel M^{+n} (C_2) : M$

➤ Nernst equation for electrodes

$$E_{right} = E^o + \frac{0.059}{n} \log C_2 \quad E_{left} = E^o + \frac{0.059}{n} \log C_1$$

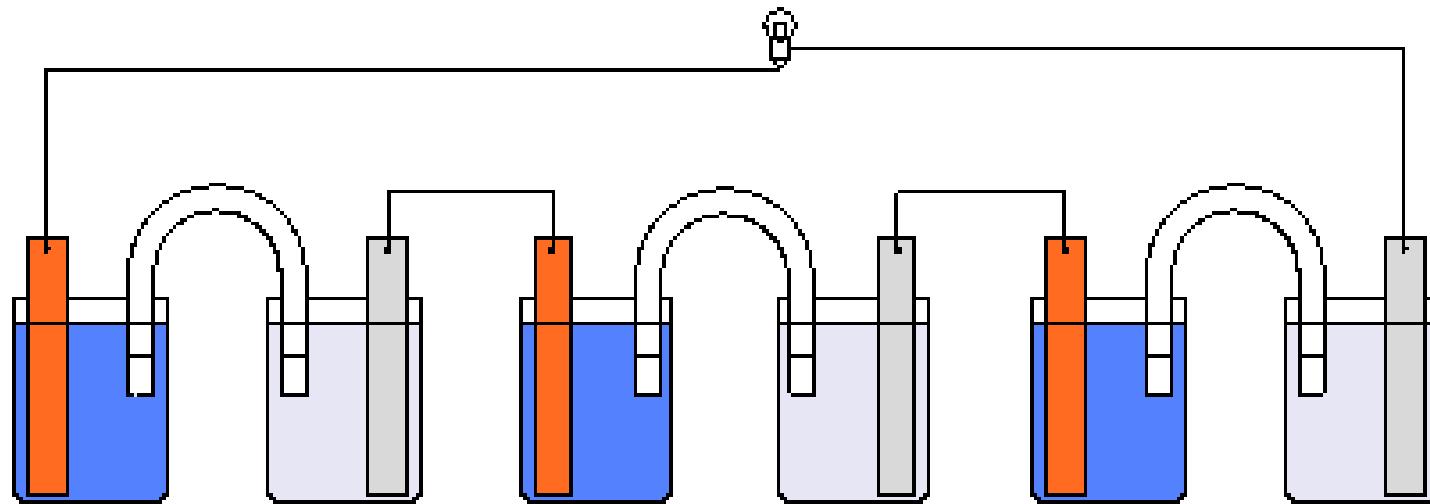
$$\therefore E_{cell} = E_{right} - E_{left}$$

$$E_{cell} = \left[E^o + \frac{0.059}{n} \log C_2 \right] - \left[E^o + \frac{0.059}{n} \log C_1 \right]$$

$$E_{cell} = \frac{0.059}{n} \log \frac{C_2}{C_1}$$

CELLS (OR) BATTERIES

- ❖ Cell is a device in which chemical energy is converted into electrical energy.
- ❖ Many cells connected in series are called battery



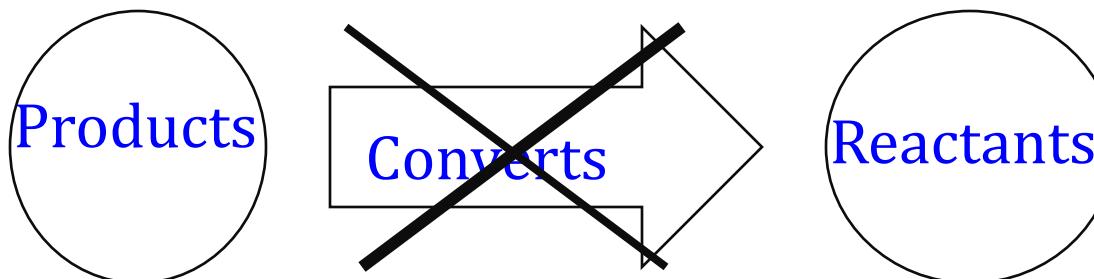
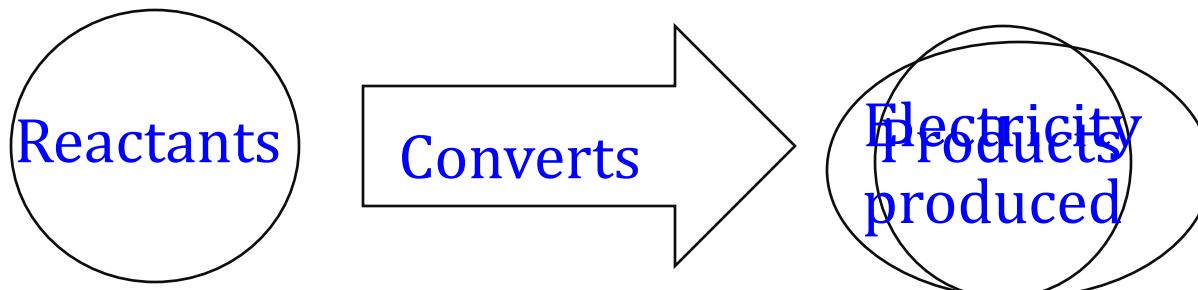
Battery of three Daniell's Cells

Cells are of two types

Primary battery or primary cells

Secondary cells or secondary battery

These reactions are irreversible

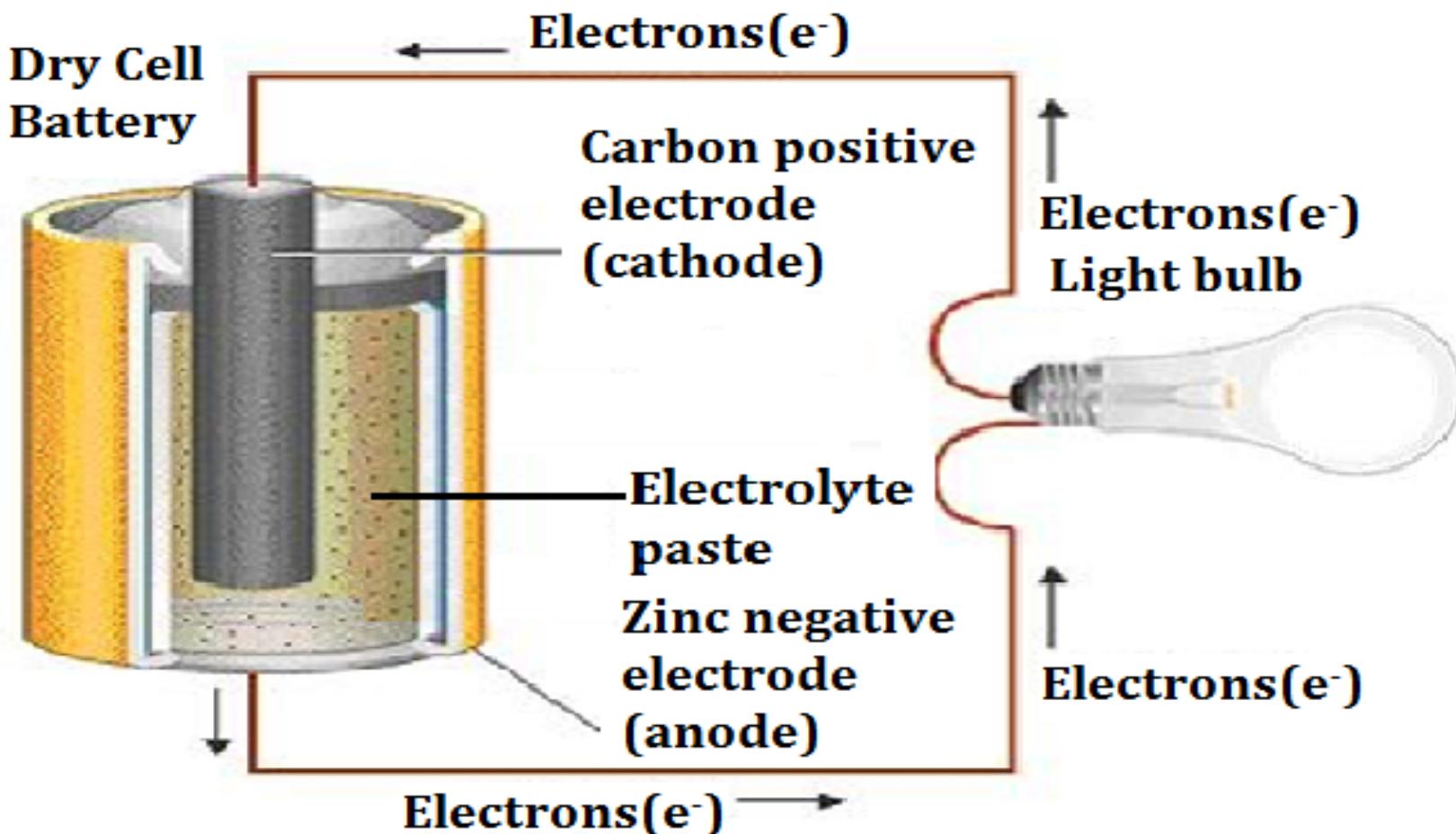


PRIMARY CELLS

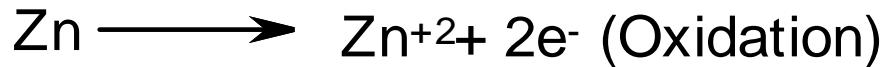
Dry or Leclanche cell

electrolyte consisting of NH_4Cl , ZnCl_2 and MnO_2

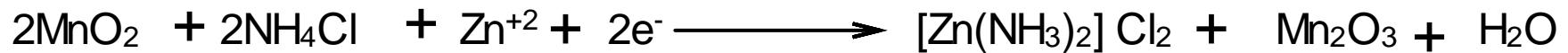
The voltage of the cell is 1.5V



At anode oxidation takes place



At cathode reduction takes place



Net reaction



Advantages

❖ Flash lights



❖ Transistor radio



❖ calculators

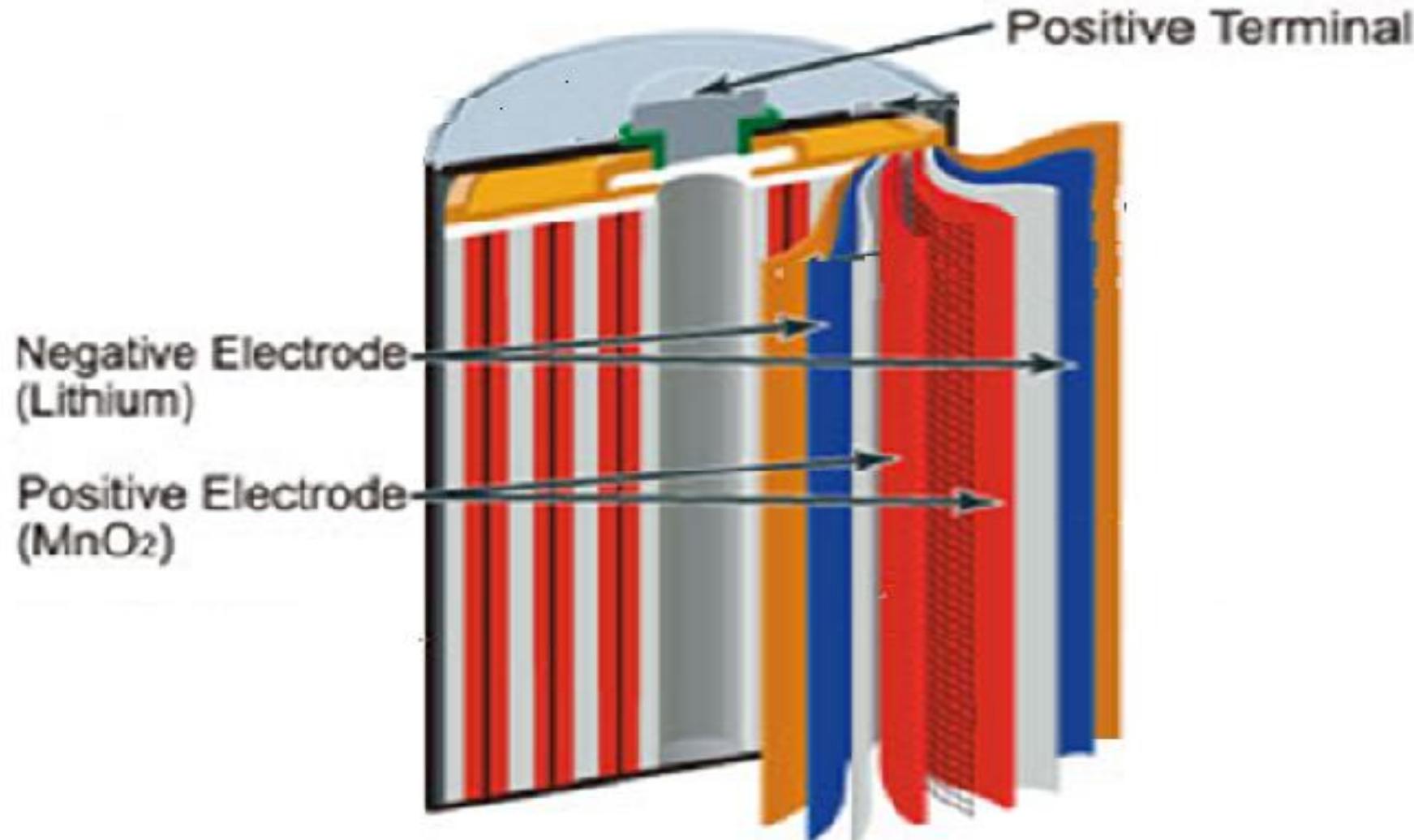


Disadvantages

Due to acidic nature cell rundown even it is not in use

Solid lithium batteries

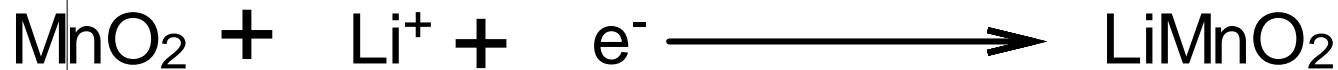
Mixture of propylene carbonate and 1,2 di methoxy ethane containing LiClO_4 acts as electrolyte



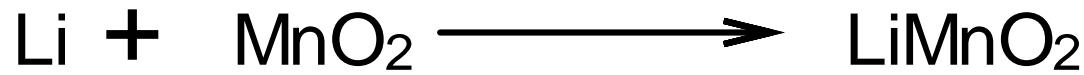
At anode oxidation takes place



At cat



Net rea



Applications

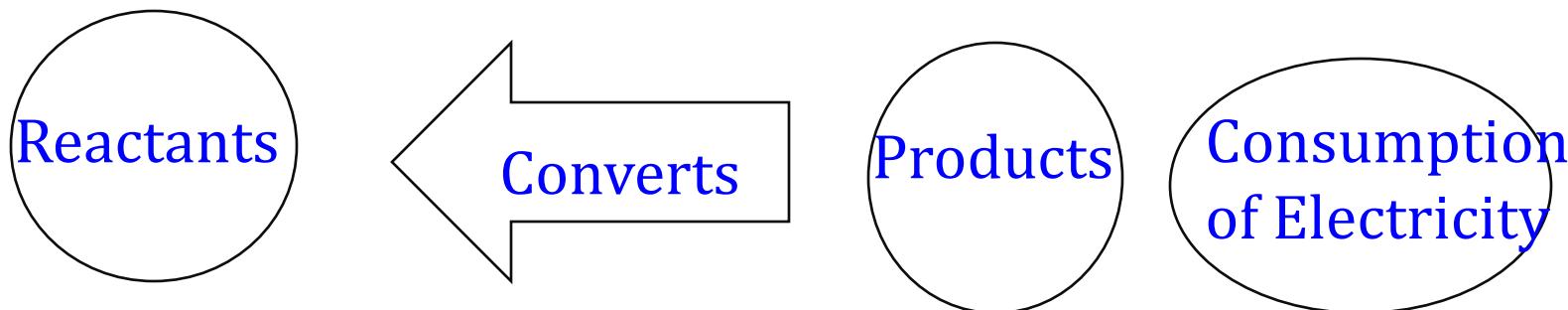
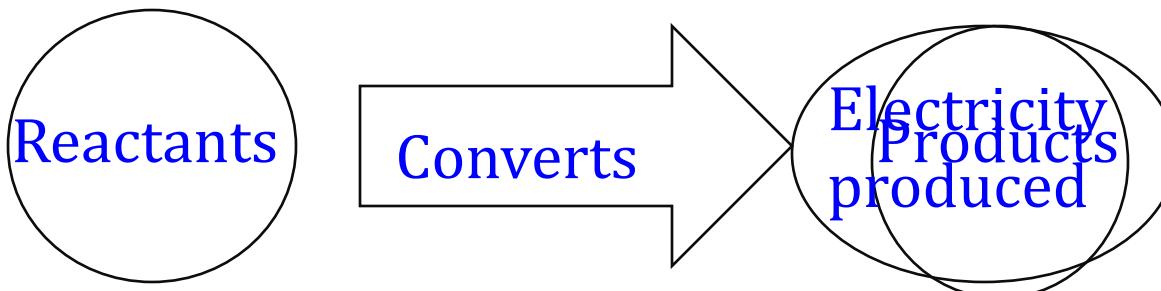
❖ Cylindrical battery used in Automatic cameras



❖ Coin type battery used in calculators, watches

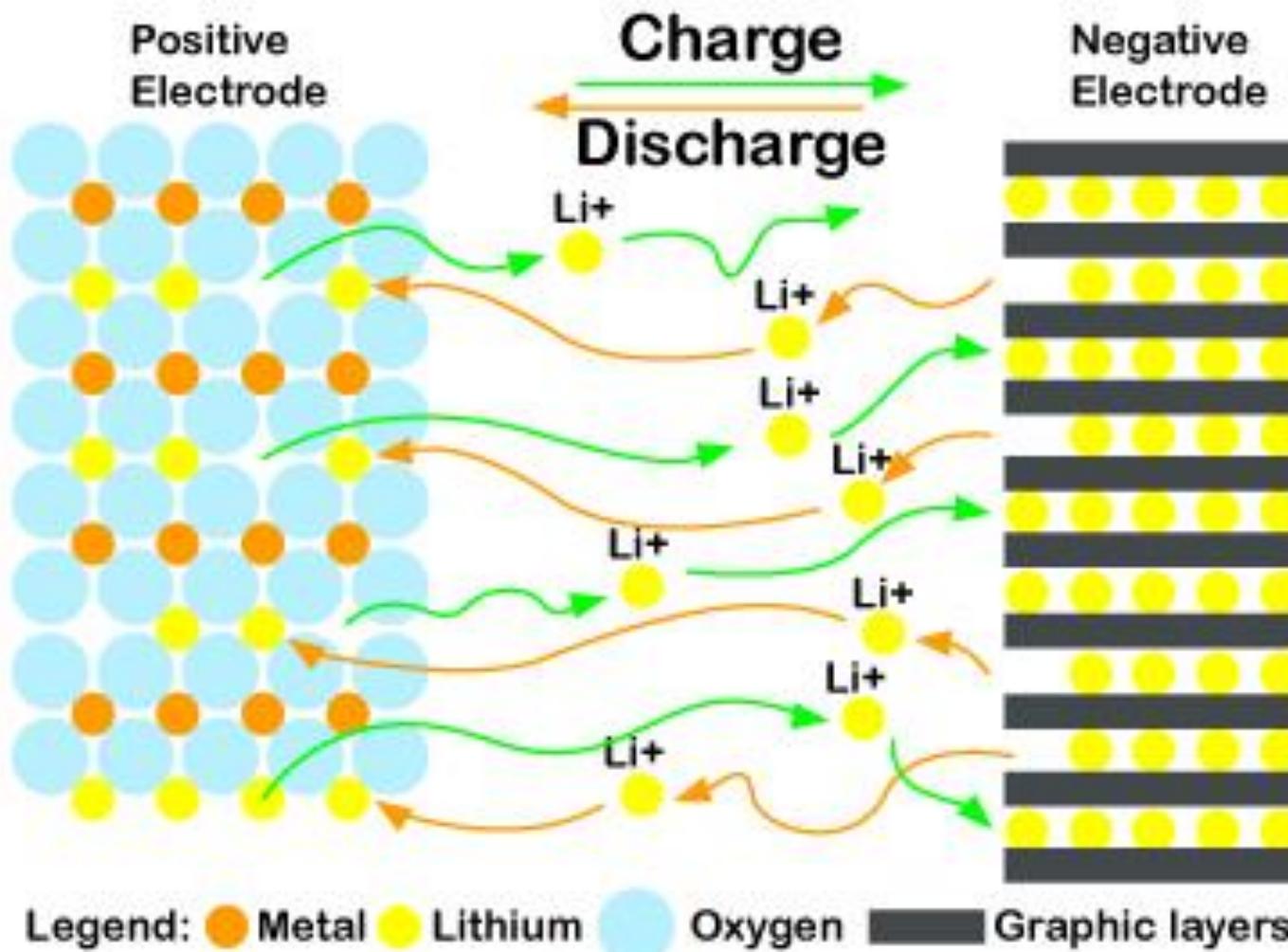
Secondary cells or secondary battery

Cell reactions are reversible



Lithium ion battery

These batteries contain lithium ions instead of metallic lithium



- ❖ In these cells, oxidation and reduction reactions does not takes place
- ❖ transport of Li^+ ions from one electrode to another electrode through the electrolyte

Charging Process



Discharging Process

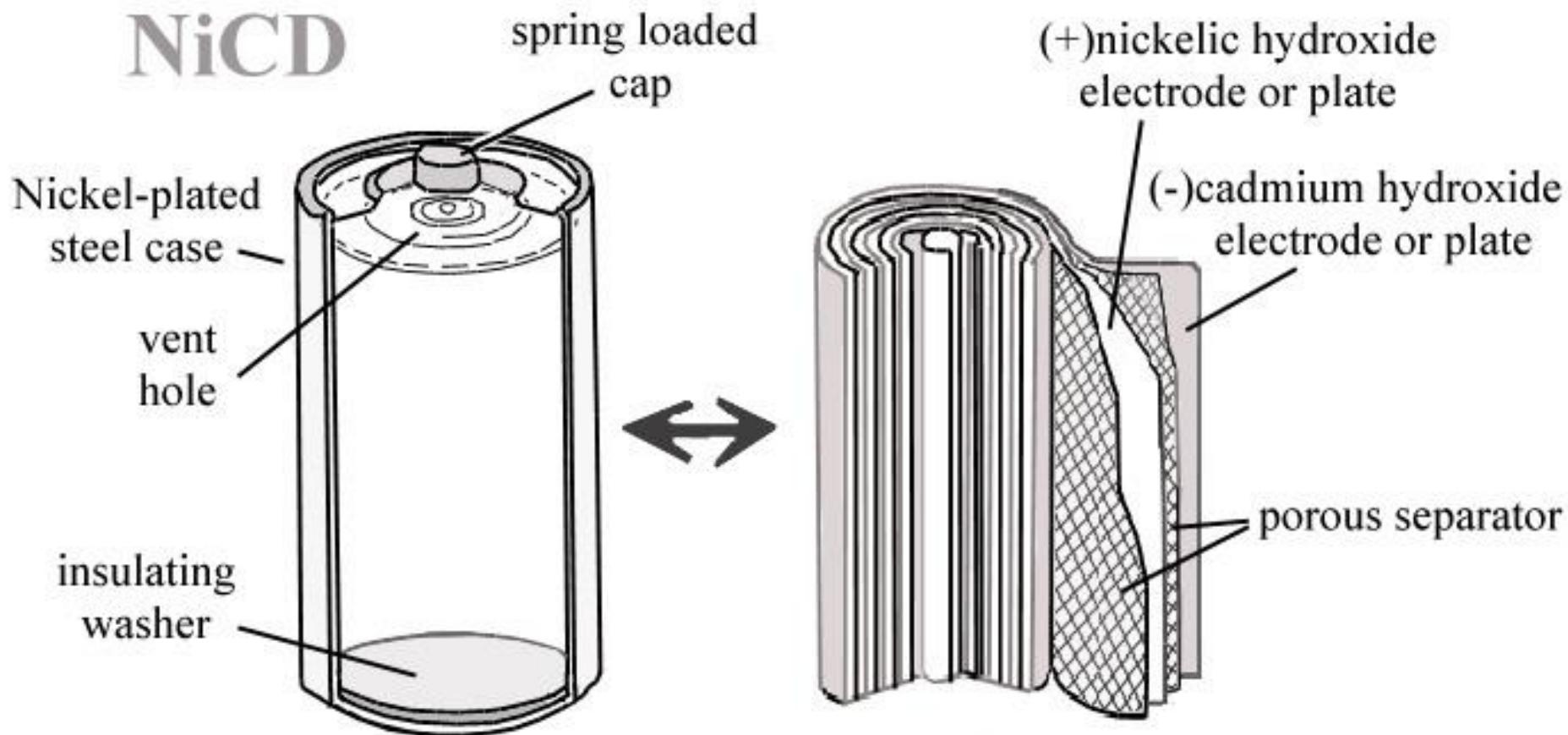


Lithium ion battery used in military ,space and medical applications

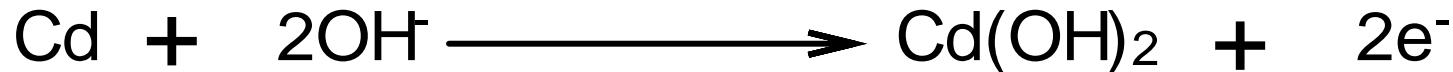


Nickel – Cadmium (Ni-Cd) battery:

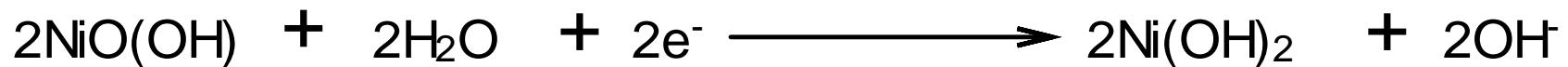
cadmium anode and a cathode composed of NiO(OH)



At anode oxidation takes place



At cathode reduction takes place



Applications

Calculators

Transistors

Cordless shavers

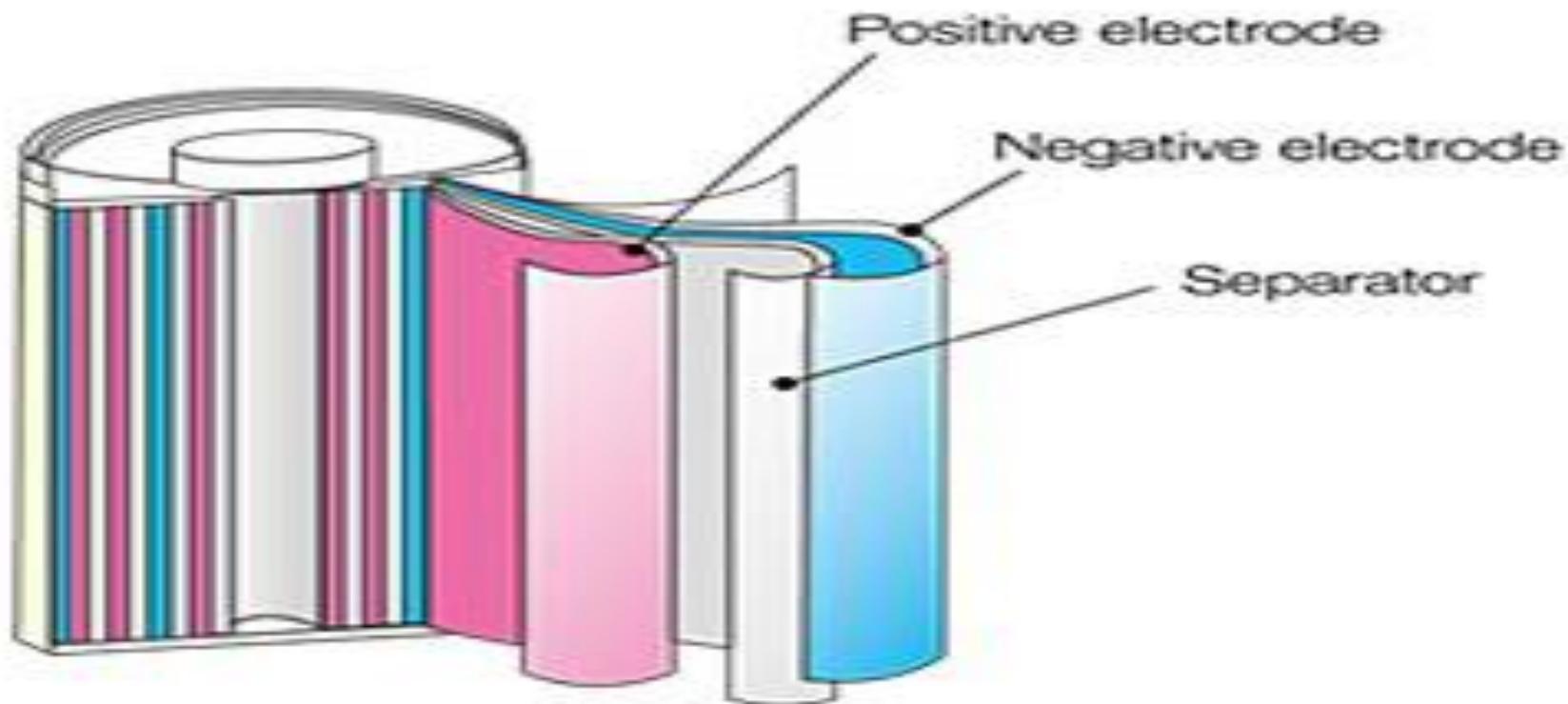
NICKEL-METALHYDRID CELL

Anode: $\text{Ni}(\text{OH})_2/\text{NiOOH}$

Cathode: M/MH

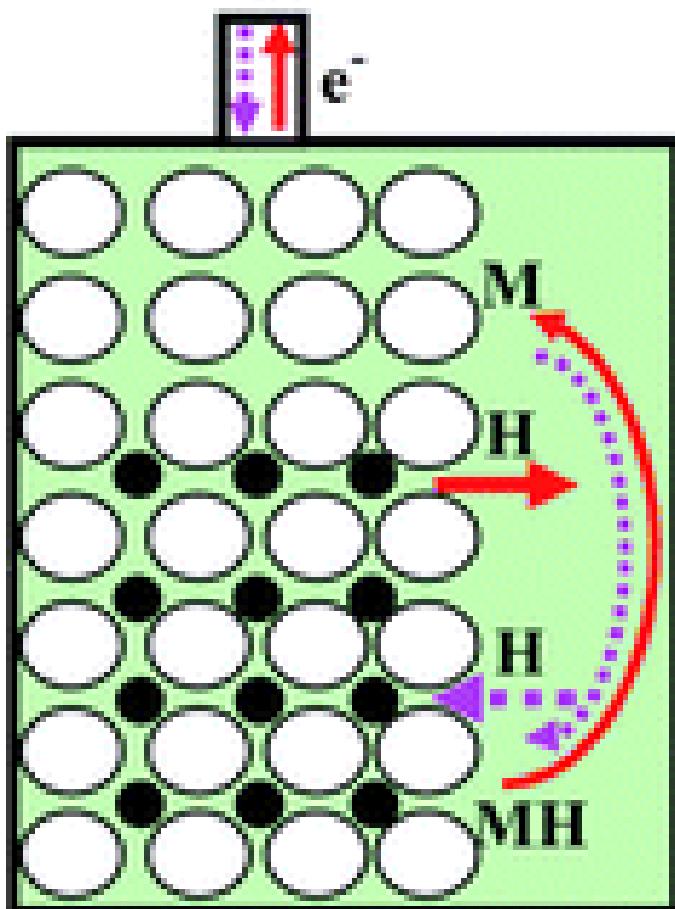
Electrolyte: KOH Solution

Conventional Nickel Metal-Hydride (Ni-MH) Cylindrical Battery

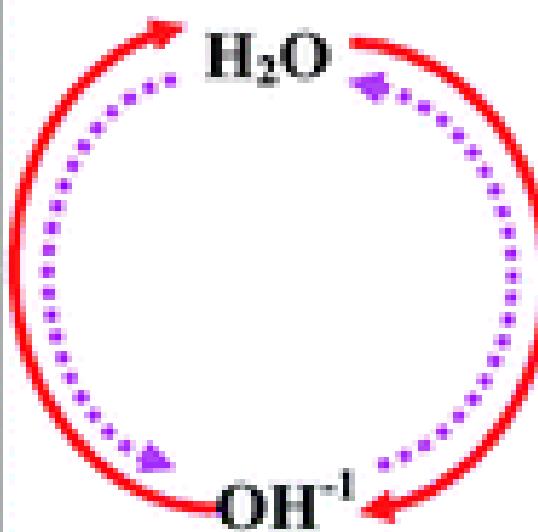


NICKEL-METALHYDRIED CELL

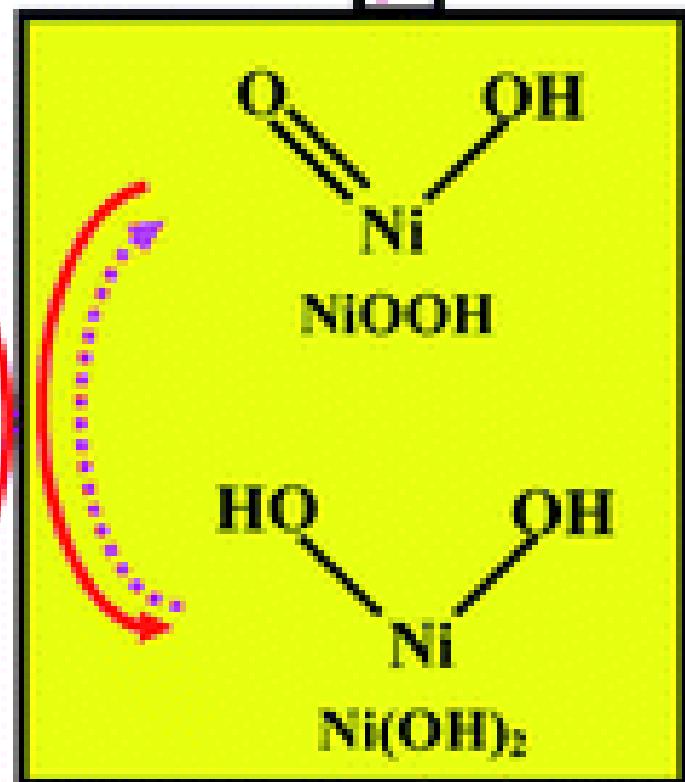
discharge



charge



e^-



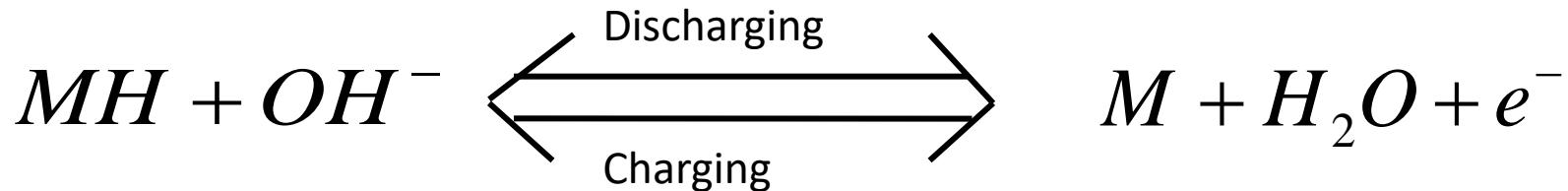
Negative electrode

Electrolyte

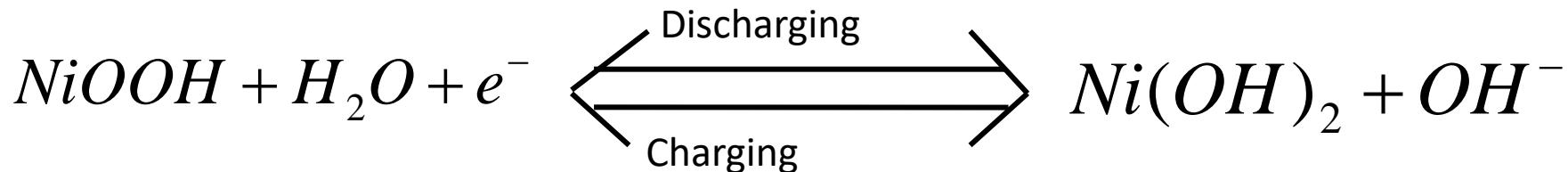
Positive electrode

NICKEL-METALHYDRIED CELL

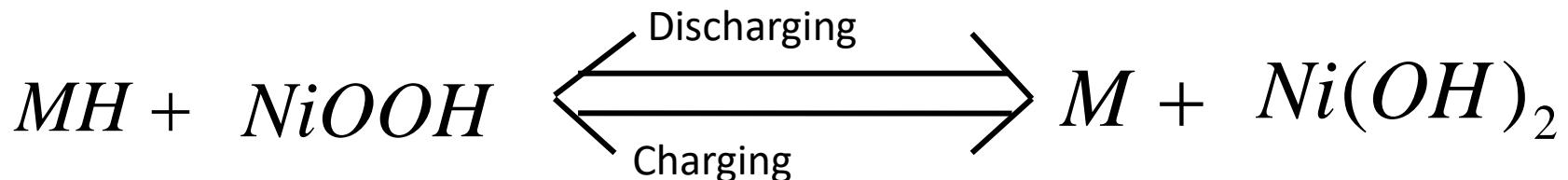
At anode



At cathode



Net reaction



NICKEL-METALHYDRIED CELL

- The out put voltage is 1.35V
- Ni-MH is high capacity
- Ni-MH is long cycle life
- Ni-MH is No maintenance

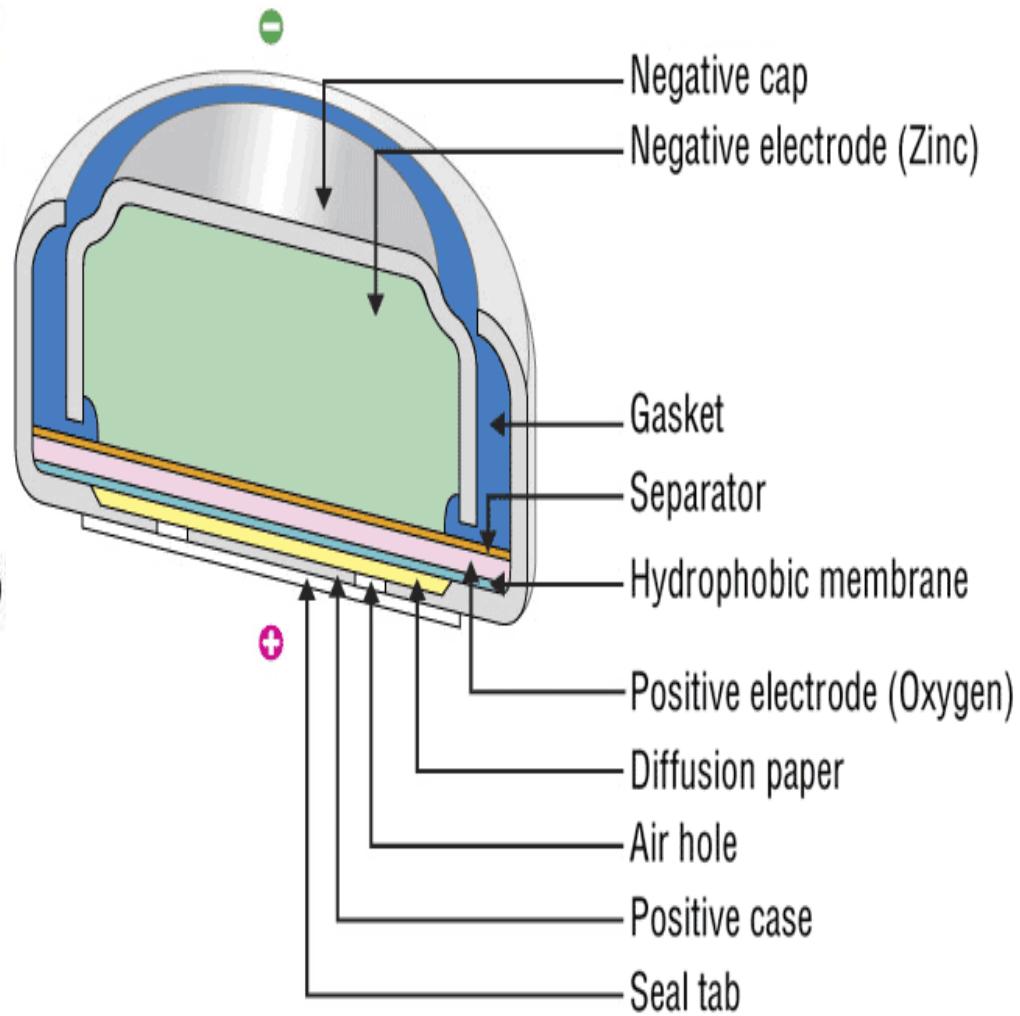
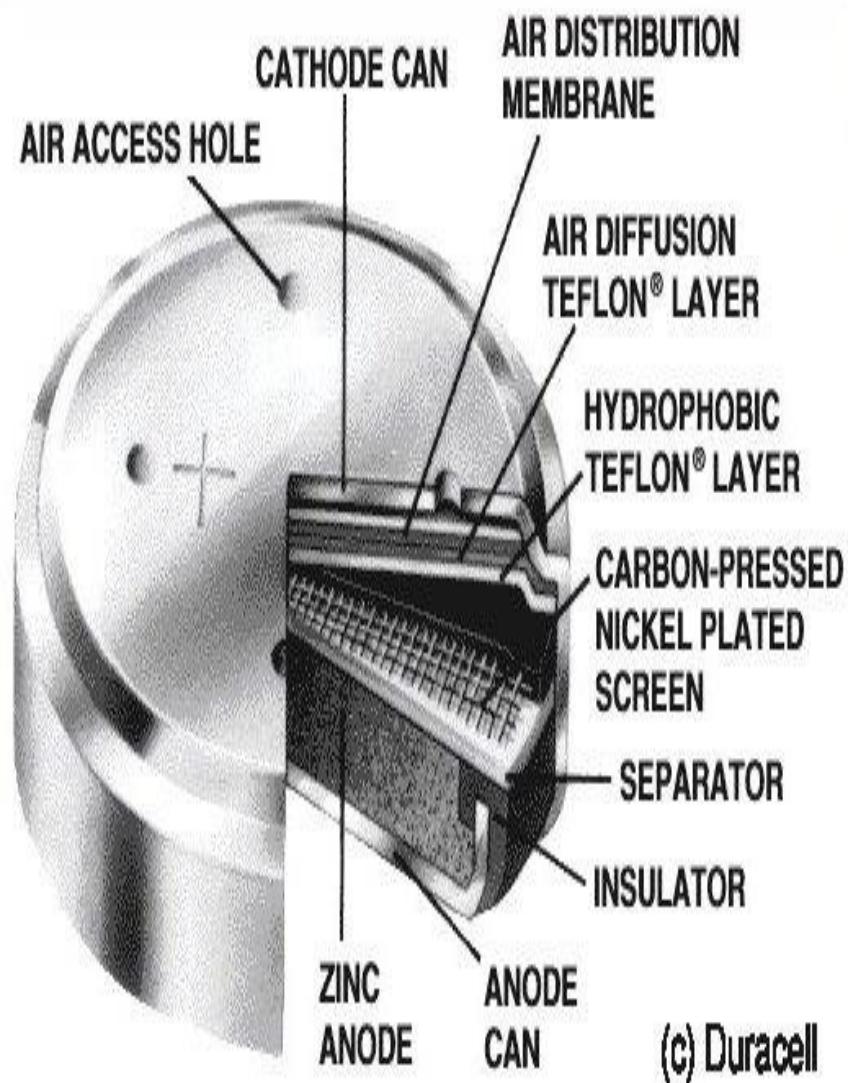
Applications:

Used in computers

Used in cell phones

Used in electronic appliances

ZINC -AIR BATTERIES

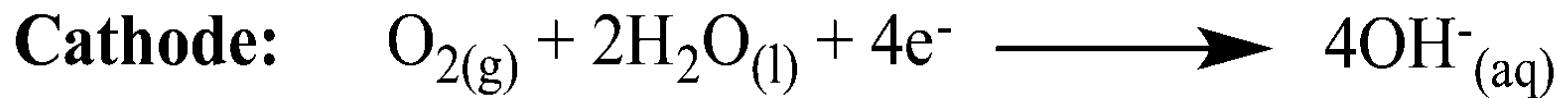
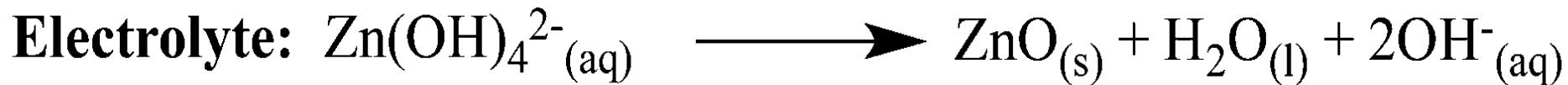
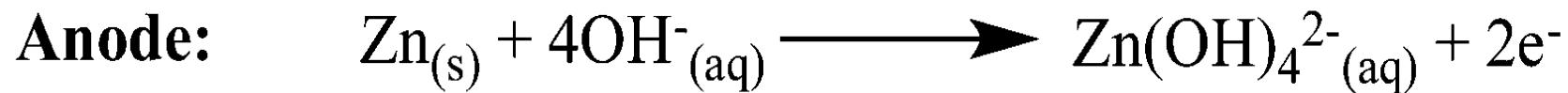


ZINC -AIR BATTERIES

Anode : Zinc

Cathode : Air

Electrolyte : KOH



Applications:



Very small battery used in hearing aids

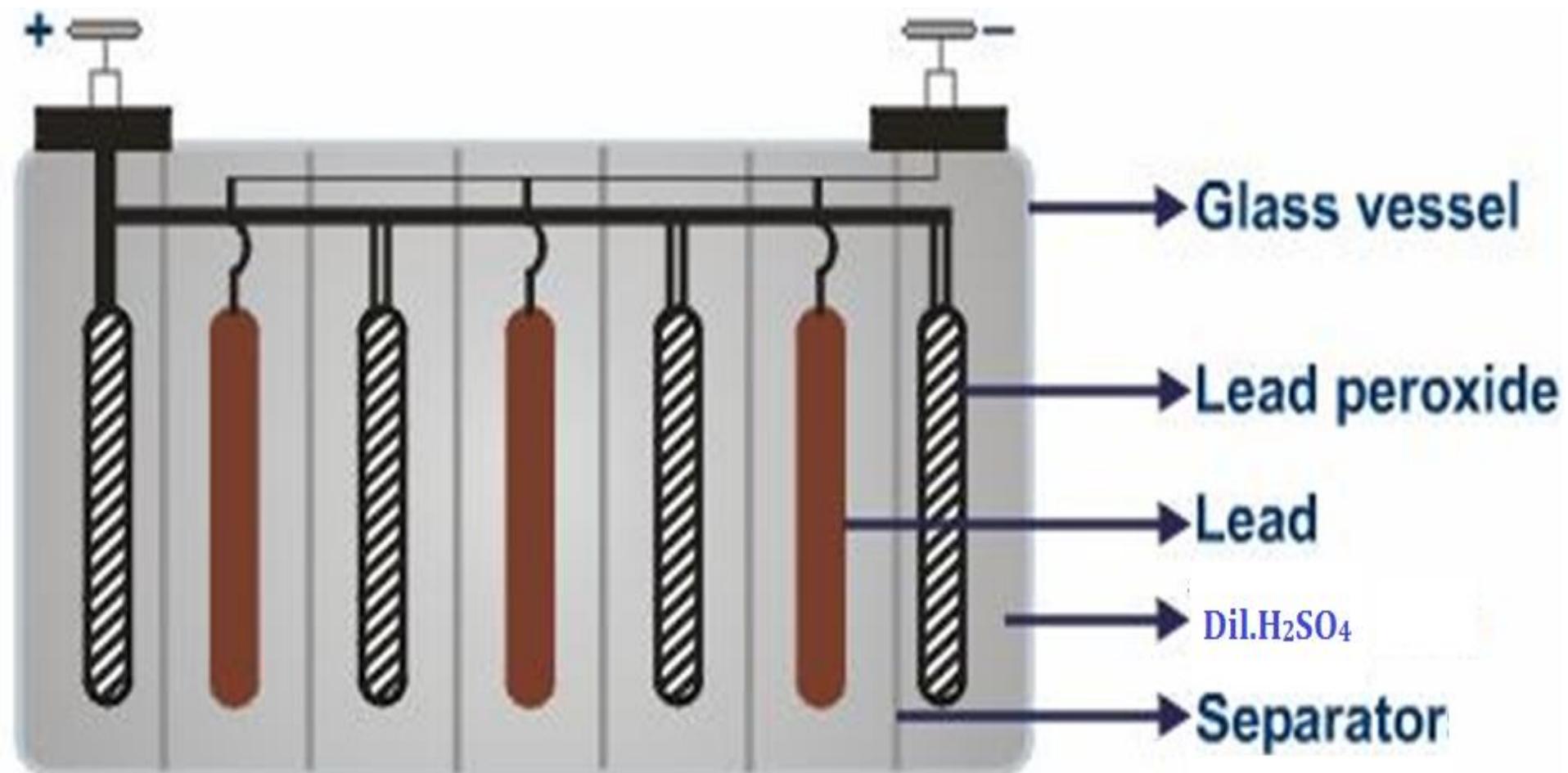


Larger battery used in cameras



Very larger battery used in electric vehicles

Lead acid storage battery



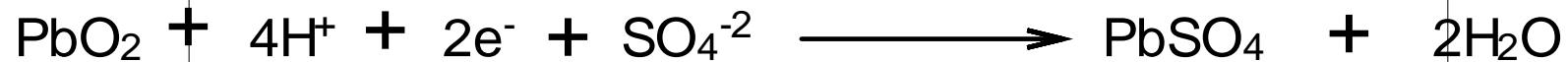
- ❖ It can acts as voltaic cell and electrolytic cell.
- ❖ Each cell has voltage 2 volts.
- ❖ Many such cells connected in series develop total potential.
- ❖ A 12V battery has six cells.

Discharging Process

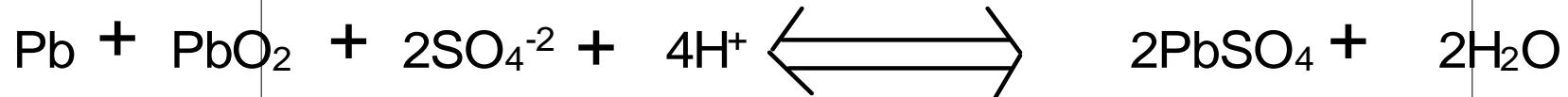
At anode



At cathode



Net reaction



Charging Process

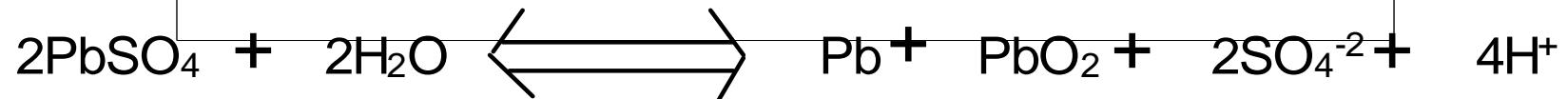
At anode



At cathode



Net reaction



These batteries are used in vehicles, telephone exchanges, power plants, electric trains, hospitals etc.

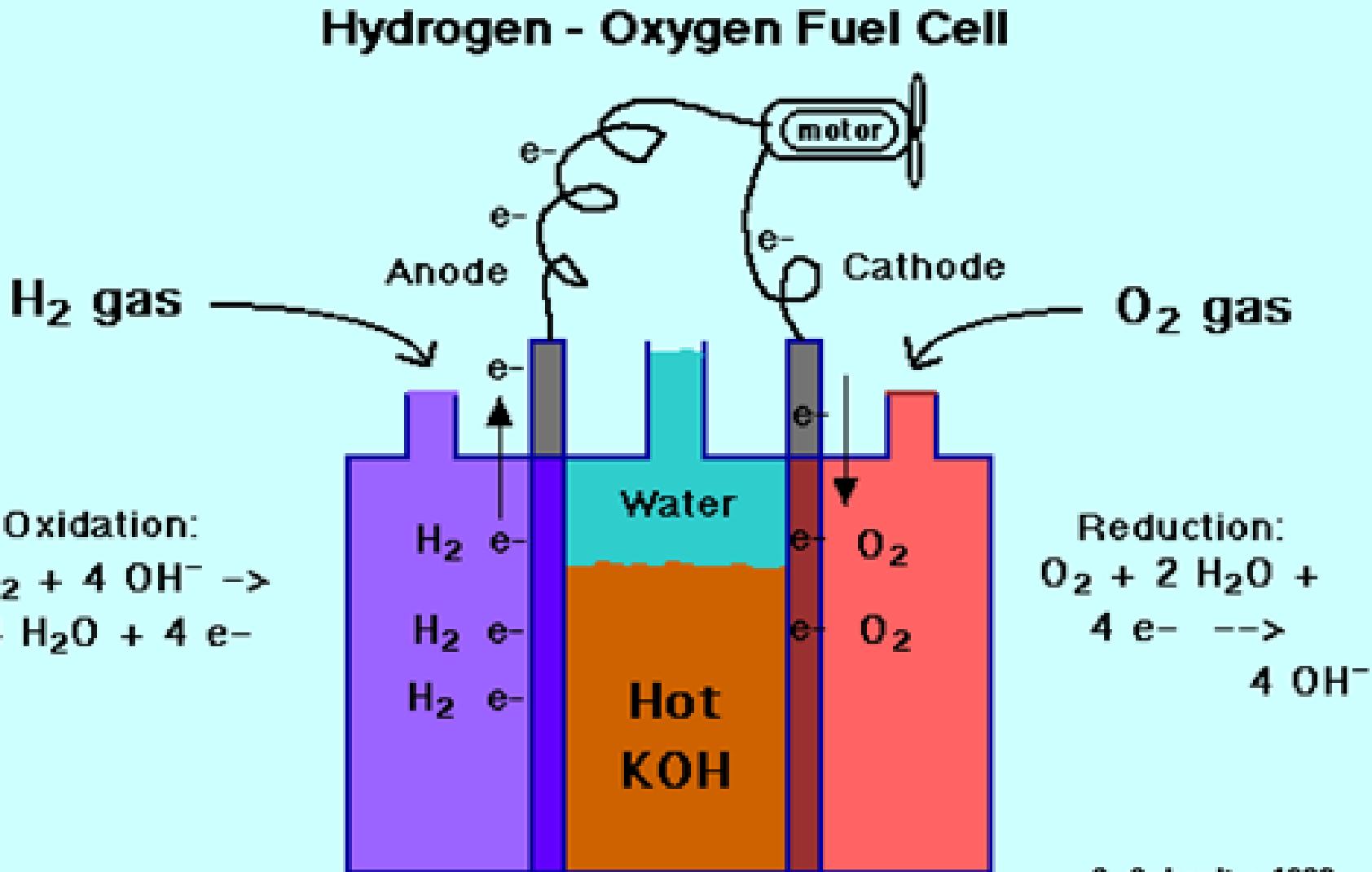


FUEL CELLS

- ❖ A fuel cell is an electrochemical cell which converts chemical energy into electrical energy by available oxidant.
- ❖ The fuel and oxidizing agents are continuously supplied to the electrodes of the cell, at which they undergo reactions.
- ❖ Fuel cells are characterized by
 - High efficiency
 - Low noise
 - Free from vibration and pollution

Hydrogen – oxygen fuel cell

The electrode consists of two porous electrodes and an electrolyte solution of 2.5% KOH with Ag or Ni.

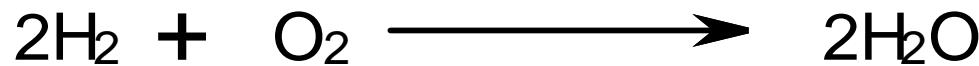


Hydrogen – oxygen fuel cell

At anode oxidation takes place

At cath

Net rea



↷ The product discharged in water and the standard EMF of the cell is $E^\circ = 1.23\text{V}$.

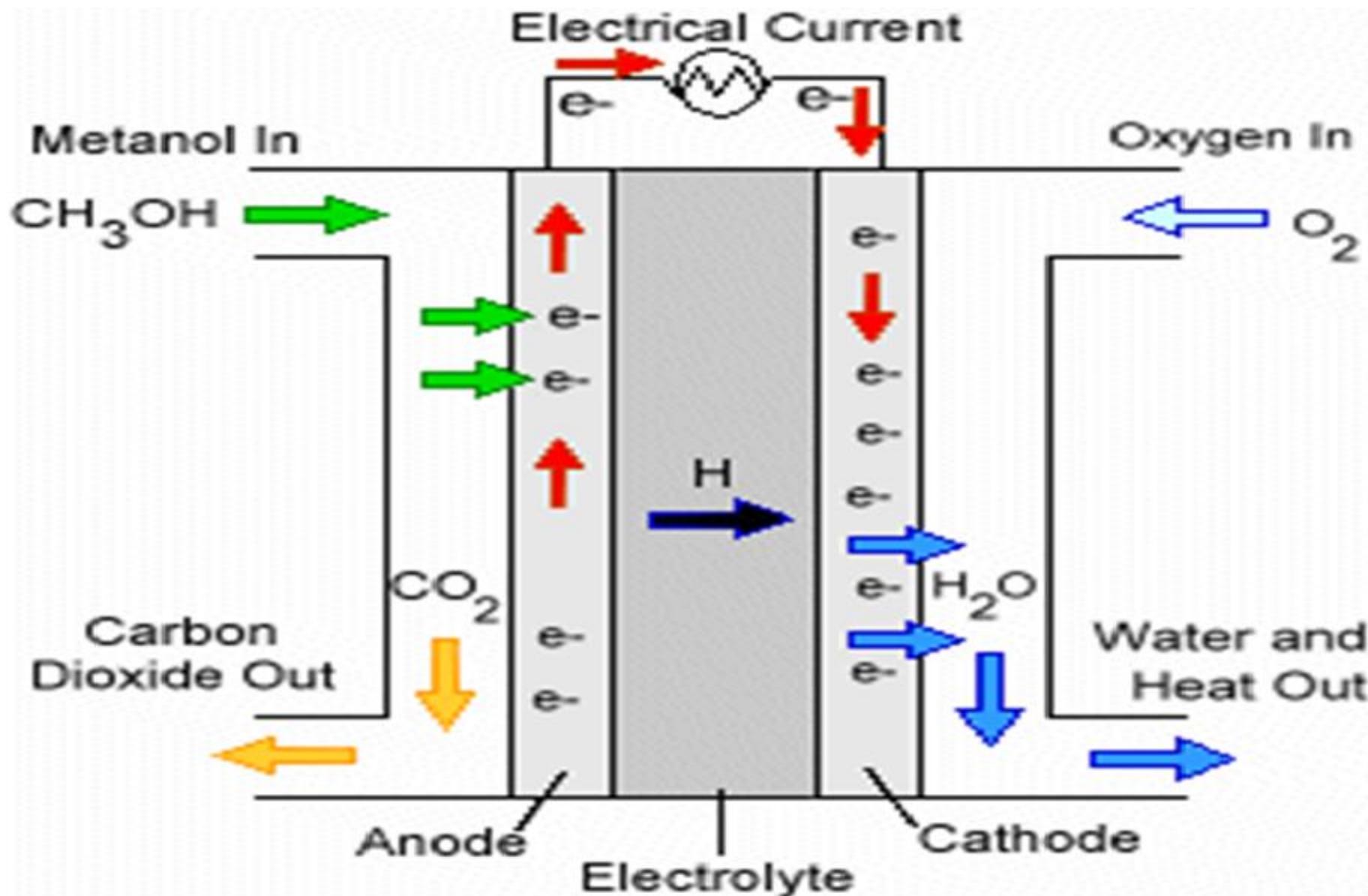
Applications

- ❖ They are used as auxiliary energy source in space vehicles, submarines etc.
- ❖ Because of light weight and pure drinking water formation, they are highly useful in space crafts.

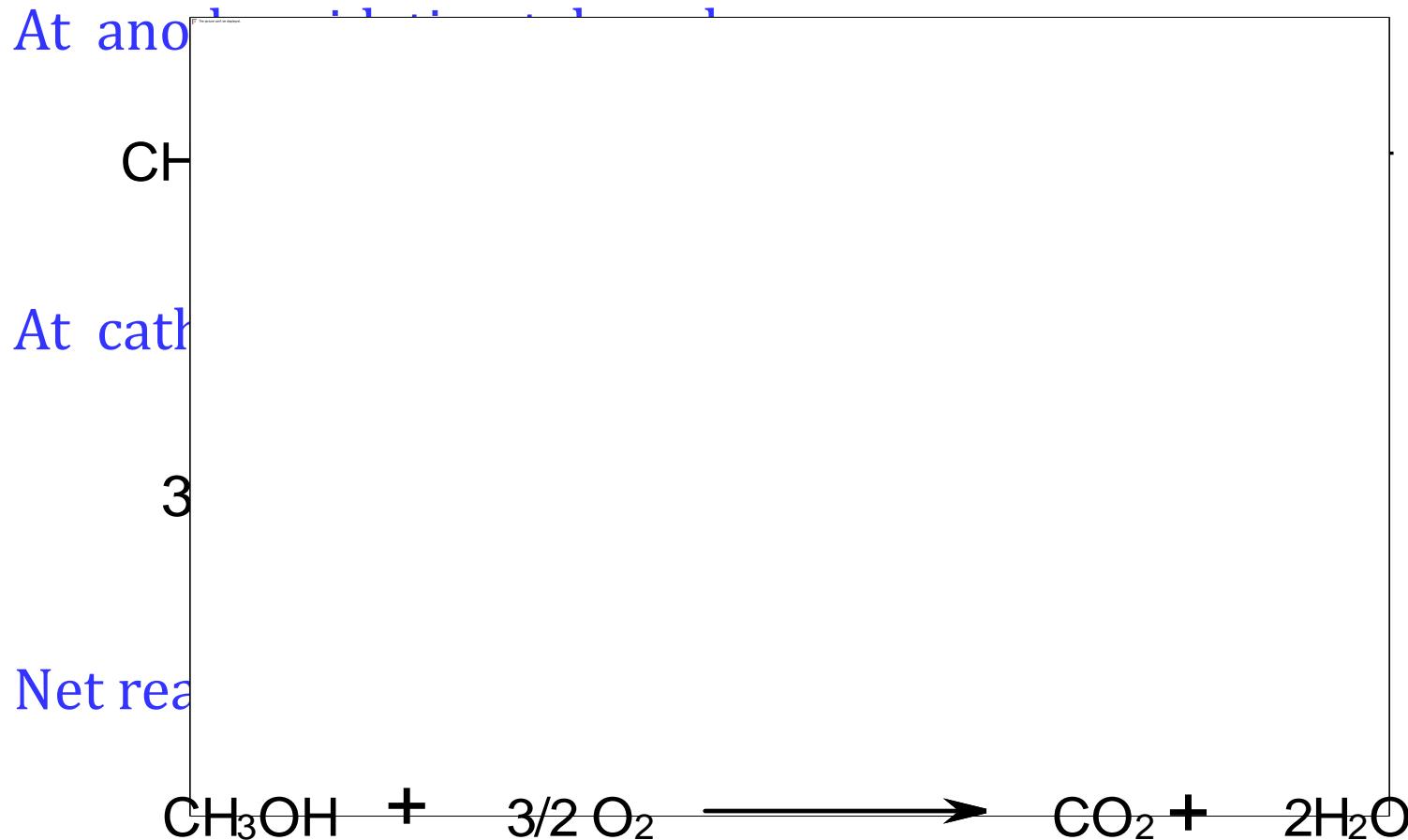
Limitations

- ❖ Life time of fuel cells is not known accurately.
- ❖ Initial cost is high.
- ❖ The distribution of H₂ is not proper.

Methyl alcohol oxygen fuel cell:



Charging Process



Limitations

- ❖ Methanol toxic and flammable
- ❖ Produce limited power

Advantages

- ❖ Storage of methanol is easy

**Instruction Material
For
The Course: Engineering Chemistry
A.Y. 2018-19
CO1**



**K L E F
Department of Chemistry**

Basic concepts of electrochemistry-Electrode Potential, Single electrode potential Galvanic cell, Measurement of Electrode Potential.

Single electrode Potential and its measurement

Introduction:

Electrochemistry is a Phenomenon which gives the relation between Chemistry and Electricity.

Single electrode Potential:

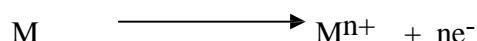
It is defined as the potential developed at the inter phase between the metal and the solution, when a metal is dipped in a solution containing its own ions. It is represented as E.

The origin of electrode Potential:

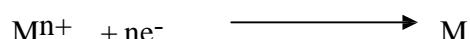
When a metal is dipped in a solution containing its own ions, the metal may undergo oxidation by loosing electrons or the metal ions in solution may undergo reduction and get deposited on the metal surface.

Consider a metal 'M' is dipped in a solution containing its ions M^{n+} .

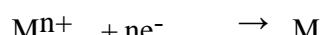
The tendency of metal to pass in to solution (oxidation) can be represented as,



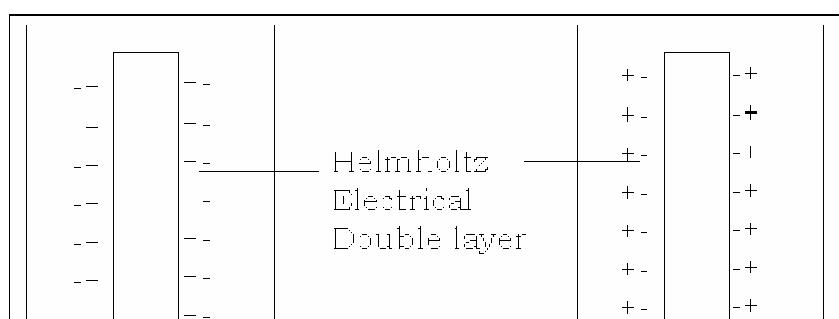
Simultaneously the metal ions from the solution tend to deposit on the metal as metal atoms (reduction)



The above two opposite tendencies will results in equilibrium as follows



When a metal undergoes oxidation it loses positive ions into solution leaving behind a layer of negative charges on its surface. This layer attracts positive charges and forms an electric double layer (EDL) because of the formation of EDL electrode potential arises.



When metal ions undergo reduction depositing metal atoms on the metallic surface the metal surface becomes positively charged. The accumulated positive charge on the metal surface attracts a layer of -ve charges and forms an electrical double layer or Helmotz EDL which causes the origin of electrode potential.

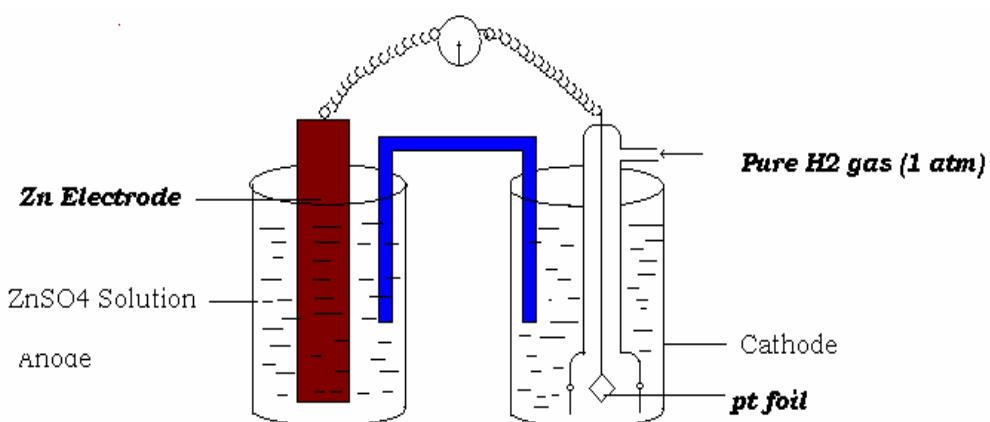
Measurement of electrode potential

The electrode potentials of any metal electrodes can be determined by using reference electrodes like standard hydrogen electrode (SHE).

The SHE is coupled with the electrode whose electrode potential is to be determined and the electrode potential of the electrode is determined by fixing the electrode potential and SHE as zero [at all temperatures]

Example: Consider the determination of Single electrode potential of Zinc electrode using Standard Hydrogen electrode.

To determine the Single electrode potential of Zinc electrode it is coupled with Standard Hydrogen electrode as follows:



The electrode potential of Zinc electrode can be calculated as

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E_{\text{SHE}} - E_{\text{Zn}}$$

$$0.76 = 0 - E_{\text{Zn}}$$

$$E_{\text{Zn}} = -0.76 \text{ V}$$

The electrode potentials can also be determined by using secondary reference electrode such as calomel electrode and Ag / AgCl electrode.

Electrochemical Cells, Reversible and Irreversible cells and Cell EMF

Electro Chemical Cell:

An electrochemical cell is a device, which is used to convert chemical energy into electrical energy and vice versa.

These electrochemical cells are classified into two types as follows.

- 1) Galvanic or Voltaic cells (Reversible): These are the electrochemical cells, which convert chemical energy into electrical energy.

Ex: Daniel cell, Dry cell, etc.

- 2) Electrolytic cell (Irreversible): These are the electrochemical cells, which are used to convert electrical energy into chemical energy.

Ex: Lead acid battery, Nickel cadmium battery etc.,

Electron Motive Force (EMF)

It is defined as the potential difference between the two electrodes of a galvanic cell which causes the flow of current from an electrode with higher reduction potential to the electrode with lower reduction potential. It is denoted as E_{cell} .

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

Problems:

- 1) Calculate emf of a cell constructed by combining Cu & Zn electrodes dipping in their respective ionic solutions. The standard electrode potential of Cu and Zn are 0.34 V and 0.76 V respectively at 298K.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{Cu}} - E_{\text{Zn}} = 0.34 - (-0.76) = 1.1 \text{ volt}$$

Applications of Nernst Equation:

Electrode potential of unknown metal can be determined using the Nernst equation.
It is used to predict the corrosion tendency of metals.

Problems:

(1) Calculate the reduction potential of Cu/Cu²⁺ electrode which is dipped in 0.5M of its own salt solution at 250 C and the standard electrode potential or its is 0.337.

Find out the emf.

$$E = E^0 + 0.0591/n \log (Cu^{2+}) \text{ Volts } n=2 ;$$

(Ans): Reduction Potential= 0.3230 V

(2) Find out the oxidation potential of Zn/Zn²⁺ which is in contact with 0.2 M of its own salt solution at 250C and the std. electrode potential is 0.763 V.

$$E = E^0 + 0.0591/n \log (Zn^{2+}) \text{ V } n=2;$$

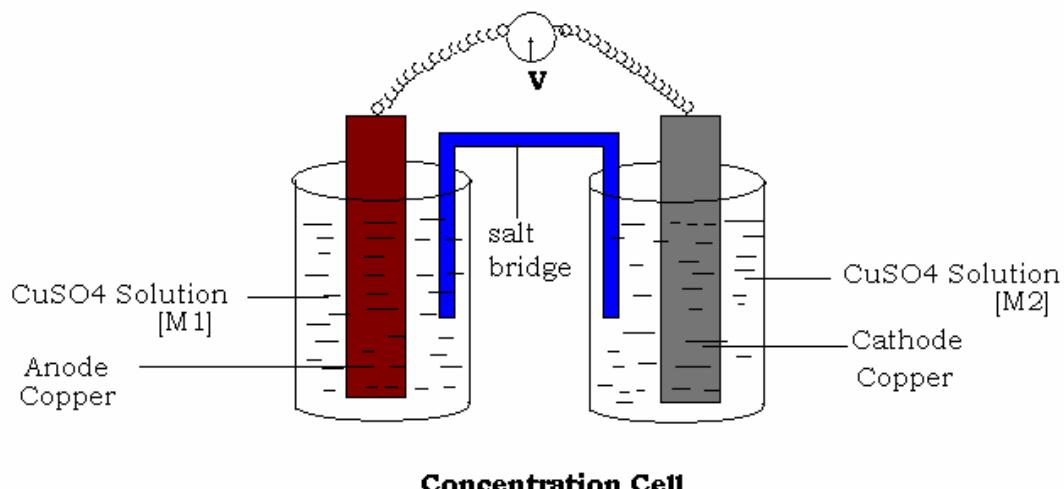
(Ans) : Oxidation potential = 0.7836 V

Concentrations cells

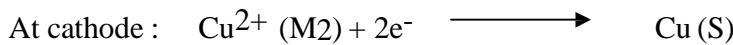
These are the galvanic cells consisting of same metal electrodes dipped in same metal ionic solution in both the half cells but are different in the concentration of the metal ions.

Ex: Consider the following concentration cell constructed by dipping two copper electrodes in CuSO₄ solutions of M₂ molar and M₁ molar where M₂ > M₁

The two half-cells are internally connected by a salt bridge and externally connected by a metallic wire through voltmeter or ammeter.



The electrode, which is dipped in less ionic concentrations solutions (M1) act as anode and undergoes oxidation. The electrode, which is dipped in more ionic concentration(M2) act as cathode and undergoes reduction.

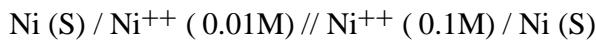


$$E \text{ of cell} = E \text{ cathode} - E \text{ anode.}$$

$$E \text{ cell} = [E^{\circ} + \frac{0.0591}{n} \log (\text{M2})] - [E^{\circ} + \frac{0.0591}{n} \log (\text{M1})]$$

Where, (M2) > (M1)

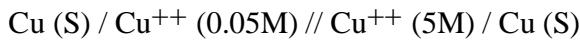
1. Calculate emf of the following concentration cell at 25° C



Where, (M2) > (M1)

$$E \text{ cell} = \frac{0.0591}{n} \log \frac{(0.1)}{(0.01)} \\ = 0.02955\text{V}$$

2. Calculate emf of the following concentration cell at 25° C



Where, (M2) > (M1)

$$E \text{ cell} = \frac{0.0591}{n} \log \frac{(5)}{(0.05)} \\ = 0.0591\text{V}$$

Reference Electrodes and pH determination using Glass Electrode

Different types of single electrodes

i) Metal-Metal ion electrode: These electrodes consist of a metal dipped in a solution of its own ions.

Example: Zn/Zn⁺⁺, Cu/Cu⁺⁺, Ag/Ag⁺

ii) Metal-Metal salt electrode

These electrodes consists of a metal in contact with its salt

Example: Calomel electrode ($\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{Cl}^-$), Silver – Silver Chloride electrode ($\text{Ag}/\text{AgCl}/\text{Cl}^-$), Lead – Lead sulphate electrode($\text{Pb}/\text{PbSO}_4/\text{SO}_4^{2-}$)

iii) Gas electrode

Example: H₂ electrode ($\text{H}_2/\text{Pt}/\text{H}^+$) Chlorine electrode ($\text{Pt}/\text{Cl}_2/\text{Cl}^-$)

iv) Amalgam electrode

Example: Lead amalgam electrode ($\text{Pb-Hg}/\text{Pb}^+$)

v) Oxidation– Reduction electrode

Example: Pt/Fe²⁺, Fe³⁺, Pt/Ce³⁺, Ce⁴⁺, Pt/Sn²⁺, Sn⁴⁺

vi) Ion selective electrode

Example: Glass electrode

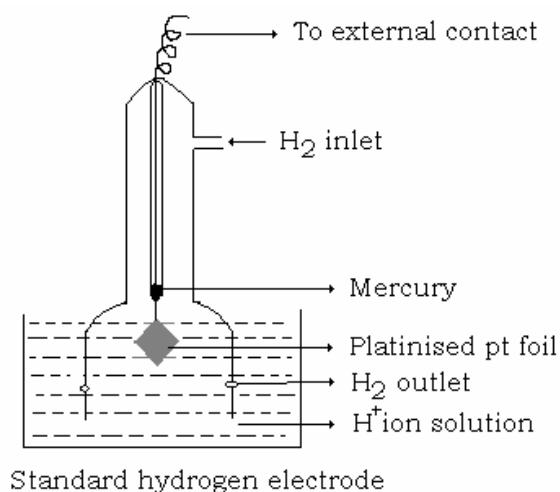
Reference Electrodes

These are the standard electrodes with reference to these, the electrode potentials of any other electrode can be determined.

The Reference Electrodes can be classified in to two types

- i) Primary reference electrodes Ex: Standard hydrogen electrode
- ii) Secondary reference electrodes Ex: Calomel and Ag/Agcl electrodes

Construction, working and limitations of standard hydrogen electrode



The standard hydrogen electrode consists of platinised platinum foil fused to the glass tube. Mercury is placed at the bottom of the tube and a copper wire is used for electrical connections. The platinum foil is immersed in a solution containing unit

molar hydrogen ions. Pure hydrogen gas is bubbled about the electrode through the H₂ gas inlet at 1atm pressure.

The electrode is represented as Pt/H₂ (g)/H⁺

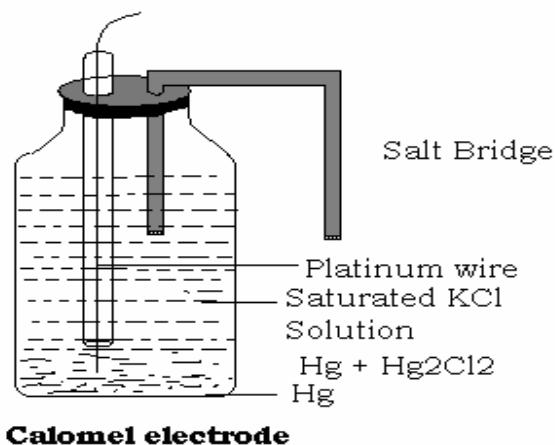
If the concentration of H⁺ is 1M, H₂ gas bubbled at 1atm pressure and at temperature 298k, then the electrode is called standard hydrogen electrode. And the electrode potential is arbitrarily fixed as zero.

The electrode reaction is:

Limitations of SHE

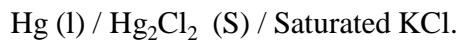
- i) The construction of SHE is difficult.
- ii) It is very difficult to maintain the concentration of H⁺ as 1M and Pressure H₂ gas at 1atm
- iii) Platinum electrode is poisoned by the impurities of the gas
- iv) It cannot be used in the presence of oxidizing agents.

Construction and working of Calomel electrode



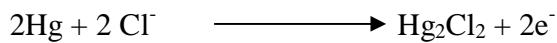
Calomel electrode consisting of a glass container at the bottom of which mercury is placed above which a layer of mercury and mercurous chloride (called calomel) is placed with 3/4th of bottle is filled with saturated KCl solution. Electrode potential

of the cell depends on the concentration of KCl used. The calomel electrode can be represented as.

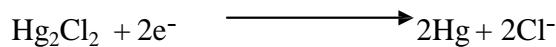


The calomel electrode acts as both anode and cathode depending upon the other electrode used. The platinum wire is used for electrical connections. Salt bridge is used to couple with other half cell.

When it acts as anode the electrode reactions is,



When it acts as cathode the electrode reaction is



Advantages of Calomel Electrode: It is simple to construct.

The electrode potential is reproducible and stable. It is used as a reference electrode.

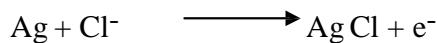
Construction and working of Silver-Silver chloride electrode.

Ag/AgCl electrode is a metal metal salt electrode. It consists of narrow glass tube at the bottom of which agar is placed above which saturated solution of KCl is placed. The silver wire is used for electrical connections and it is coated electrolytically with AgCl. The cell can be

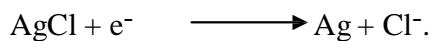
Represented as: $\text{Ag(s)} / \text{AgCl(s)} / \text{Saturated KCl}.$

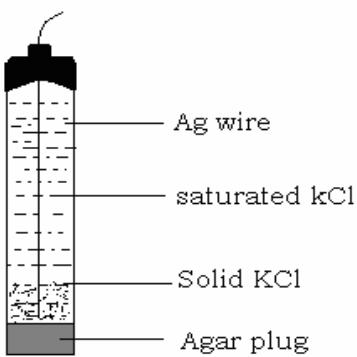
Electrode acts as both anode and cathode depending on the other electrode used.

When it acts as anode the electrode reaction is



When it acts as cathode the electrode reaction is



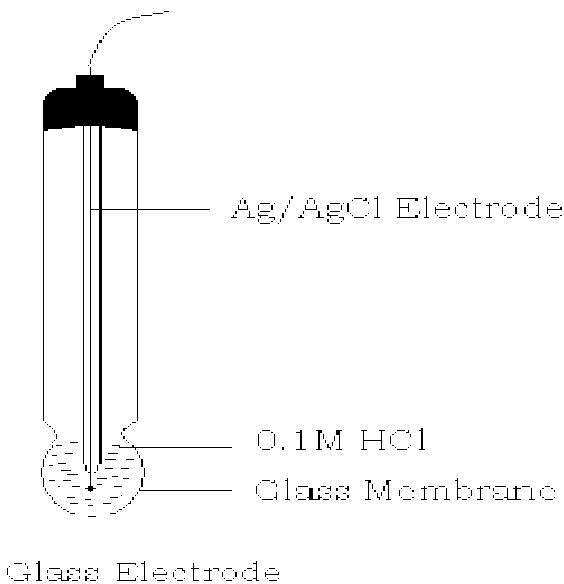


Ag/AgCl Electrode

Ion Selective Electrodes

These are the electrodes, which responds to specific ions only and develop potential against that ion while ignoring the other ions present in the solution.

Ex: Glass electrode.



Glass electrode is a pH sensitive electrode widely used for pH determinations. It is consisting of a long glass tube at the bottom of which a thin and delicate glass bulb, which made up of special type of glass (12 % Ba₂O, 6% of CaO, 72% of SiO₂) with low melting point and high electrical conductance is used. The glass bulb is filled

with 0.1M HCl and Ag – AgCl is used as a internal reference electrode. A platinum wire is used for electrical contact. The glass electrode can be represented as:



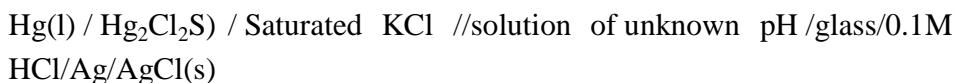
$$E_{\text{Glass}} = E^{\circ}_{\text{Glass}} + 0.0591 \log [\text{H}^+]$$

$$= E^{\circ}_{\text{Glass}} - 0.0591 \text{ pH}$$

Determination of pH using glass electrode.

To determine pH of unknown solution the glass electrode is combined with secondary reference electrode such as calomel electrode and the glass - calomel electrode assembly is dipped in the solution whose pH is to be determined. The two electrodes are connected to potentiometer or pH meter.

The combined electrodes can be represented as.



The emf of the above cell is given by

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

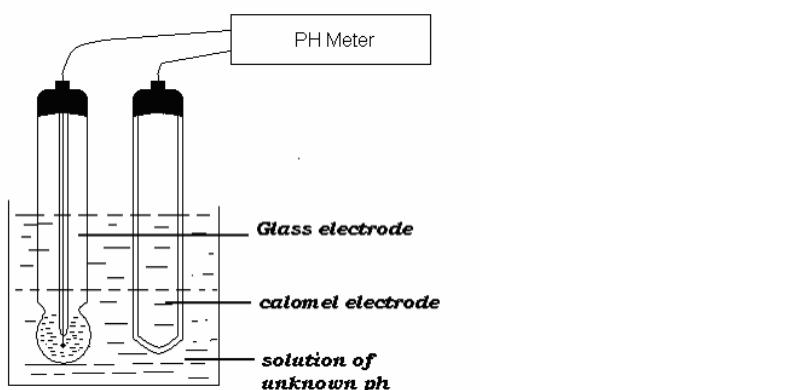
$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{glass}}$$

$$= E_{\text{SCE}} - E_G$$

$$= 0.2422 - (E^{\circ}_{\text{Glass}} - 0.0591 \text{ pH}) \quad [E_G = E^{\circ}_G - 0.0591 \text{ pH}]$$

$$E_{\text{cell}} = 0.2422 - E^{\circ}_G + 0.0591 \text{ pH}$$

$$\text{pH} = E_{\text{cell}} + E^{\circ}_G - 0.2422/0.0591$$

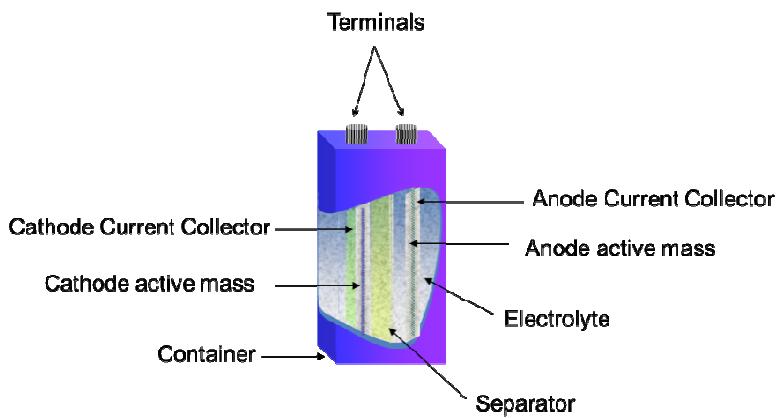


Session-6

Introduction to Batteries and Chemistry of Primary Battery (Hg-Battery)

A **battery** is an Electrochemical cell or often several electrochemical cells which are connected in series to produce a constant voltage to run portable goods.

Principle Components of a Battery



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Mainly batteries are of three types:

- 1) Primary Battery is the one in which cell reactions are irreversible.

E.g. Lechlaunche cell, Zn-Carbon Battery, Hg-Battery

- 2) Secondary Battery is the one in which cell reactions can be reversed by passing external emf in opposite direction. i.e. it can be used for many cycles of charging and discharging.

E.g. Lead – Acid battery, Ni-metal-hydride (NiMH) etc.

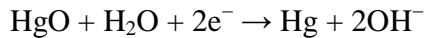
- 3) Flow battery is the one in which all the constituents of the battery flow throughout the battery.

E.g. Hydrogen-Oxygen Fuel cell.

Primary Cell (Mercury Battery)

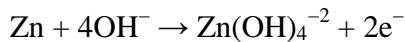
Mercury batteries use either pure mercury (II) oxide (HgO)—also called mercuric oxide—or a mixture of HgO with manganese dioxide (MnO_2) as the cathode. Mercuric

oxide is a non-conductor, so some graphite is mixed with it; the graphite also helps prevent collection of mercury into large droplets. The half-reaction at the cathode is:



with a standard potential of +0.0977 V vs. NHE.

The anode is made of zinc (Zn) and separated from the cathode with a layer of paper or other porous material soaked with electrolyte; this is known as a salt bridge. Two half-reactions occur at the anode. The first consists of an electrochemical reaction step:



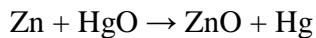
followed by the chemical reaction step:



yielding an overall anode half-reaction of:



The overall reaction for the battery is:



In other words, during discharge, zinc is oxidized (loses electrons) to become zinc oxide (ZnO) while the mercuric oxide gets reduced (gains electrons) to form elemental mercury. A little extra mercuric oxide is put into the cell to prevent evolution of hydrogen gas at the end of life.

Secondary Battery (Lead Acid and Nickel metal hydride)

Storage cell: it is the one which can act both as voltaic cell and electrolytic cell. When it functions as voltaic cell, it supplies electric current and the process is known as discharging. When it functions as electrolytic cell, it receives electric current and this process is known as charging. So it can be used for a large no. of cycles of charging and discharging. The best example for storage cell is lead acid battery or lead acid accumulator.

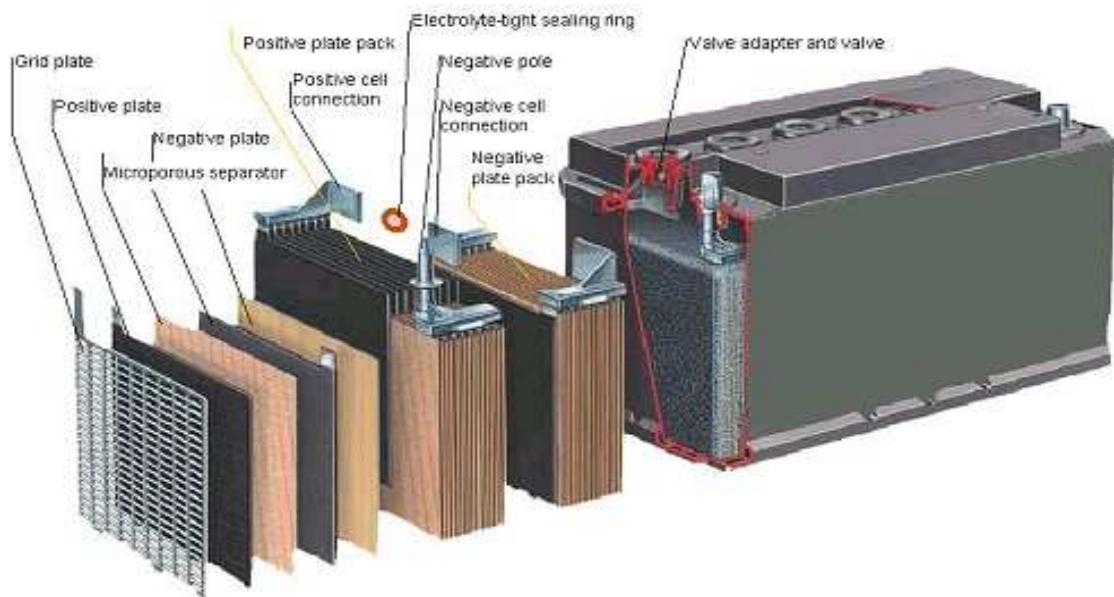
1. Lead-acid battery: Lead-acid is the oldest rechargeable battery in existence. Invented by the French physician Gaston Planté in 1859, lead-acid was the first rechargeable battery for commercial use. 150 years later, we still have no cost-effective alternatives for cars, wheelchairs, scooters, golf carts and UPS systems.

Construction: Large number of anodes and cathodes are arranged alternatively in a series separated by insulators as shown above. The entire set up is immersed in dilute sulphuric acid solution.

Anode: lead plate

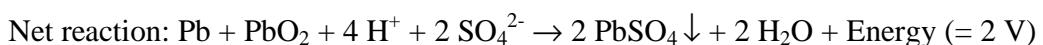
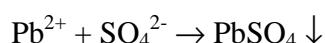
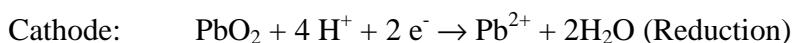
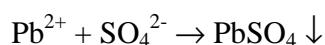
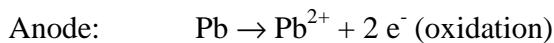
Cathode: lead dioxide plate

Electrolyte: 25% H_2SO_4 solution



Discharging:

Reactions taking place during discharging: During discharging, it acts as voltaic cell and supplies electrical energy.



The following points can be noticed from the above reaction:

- The concentration of sulphuric acid decreases in course of reaction.
- Both the electrodes are covered with lead sulphate.
- As lead sulphate is insoluble in sulphuric acid, it acts as a protective layer and prevents the further corrosion of lead.

As the lead sulphate deposited at both the electrodes is solid, the cell reactions can easily be reversed by passing emf just above the voltage of the cell i.e. $> 2 \text{ V}$.

Charging:



Application: Car battery

2. Nickel Metal Hydride (NiMH)

NiMH Principles of Operation

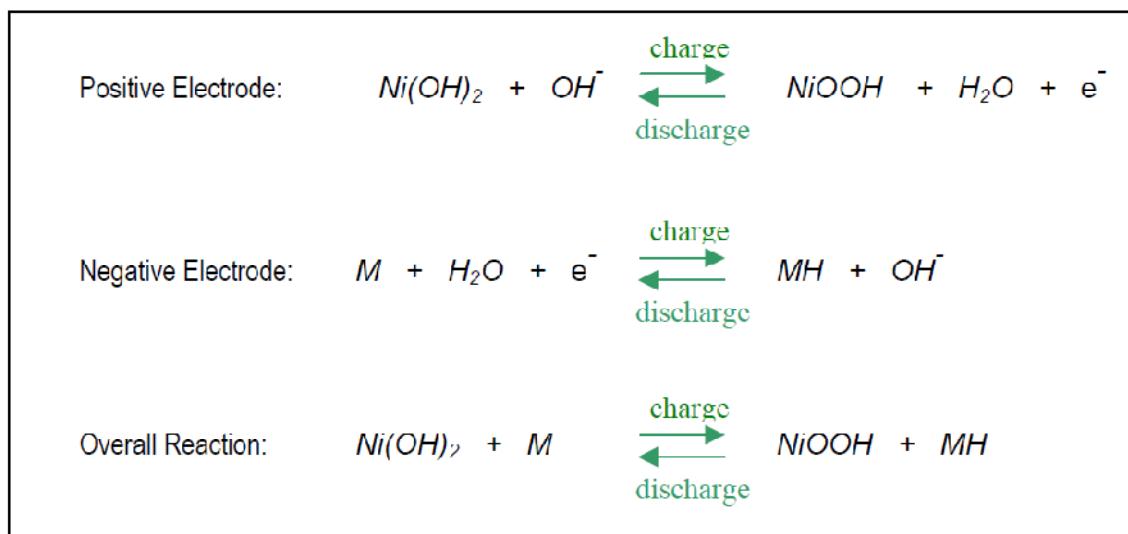
The principles in which NiMH cells operate are based on their ability to absorb, release, and transport (move) hydrogen between the electrodes within the cell. The following sections will discuss the chemical reactions occurring within the cell when charged and discharged and the adverse effects of overcharge and overdischarge conditions.

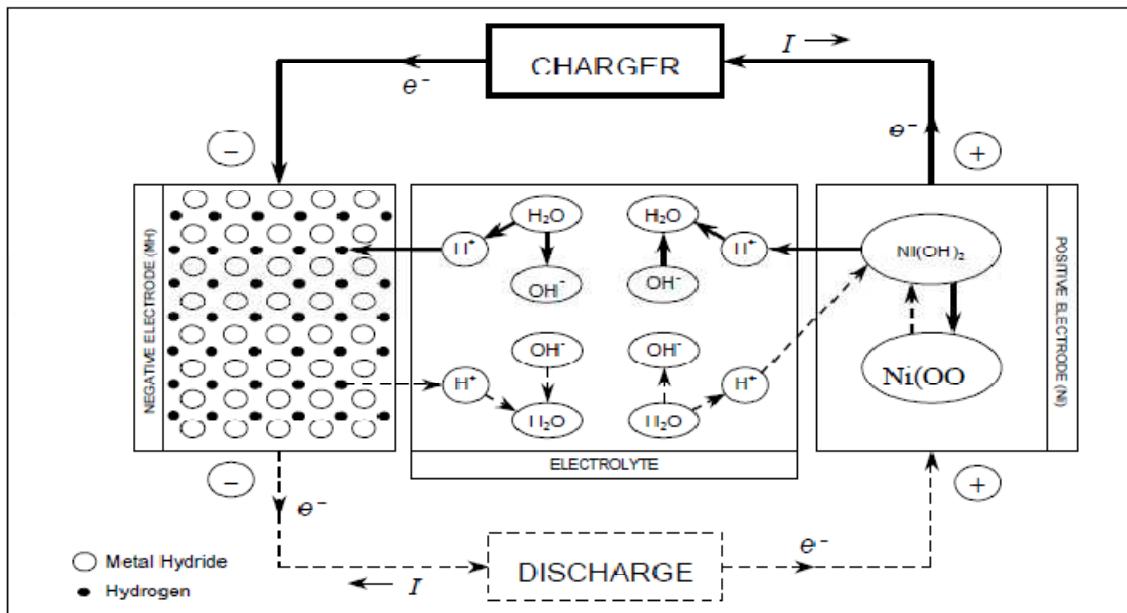
The success of the NiMH battery technology comes from the rare earth, hydrogen-absorbing alloys (commonly known as Misch metals) used in the negative electrode. These metal alloys contribute to the high energy density of the NiMH negative electrode that results in an increase in the volume available for the positive electrode. This is the primary reason for the higher capacity and longer service life of NiMH batteries over competing secondary batteries.

Charging Chemical Reaction

When a NiMH cell is charged, the positive electrode releases hydrogen into the electrolyte. The hydrogen in turn is absorbed and stored in the negative electrode. The reaction begins when the nickel hydroxide (Ni(OH)_2) in the positive electrode and hydroxide (OH^-) from the electrolyte combine.

This produces nickel oxyhydroxide (NiOOH) within the positive electrode, water (H_2O) in the electrolyte, and one free electron (e^-). At the negative electrode the metal alloy (M) in the negative electrode, water (H_2O) from the electrolyte, and an electron (e^-) react to produce metal hydride (MH) in the negative electrode and hydroxide (OH^-) in the electrolyte.





Li-ion battery, H₂-O₂ Fuel cell

Lithium ion Battery

A lithium-ion battery (sometimes Li-ion battery or LIB) is a family of rechargeable battery types in which lithium ions move from the negative electrode to the positive electrode during discharge, and back when charging. Chemistry, performance, cost, and safety characteristics vary across LIB types. Unlike lithium primary batteries (which are disposable), lithium-ion electrochemical cells use an intercalated lithium compound as the electrode material instead of metallic lithium.

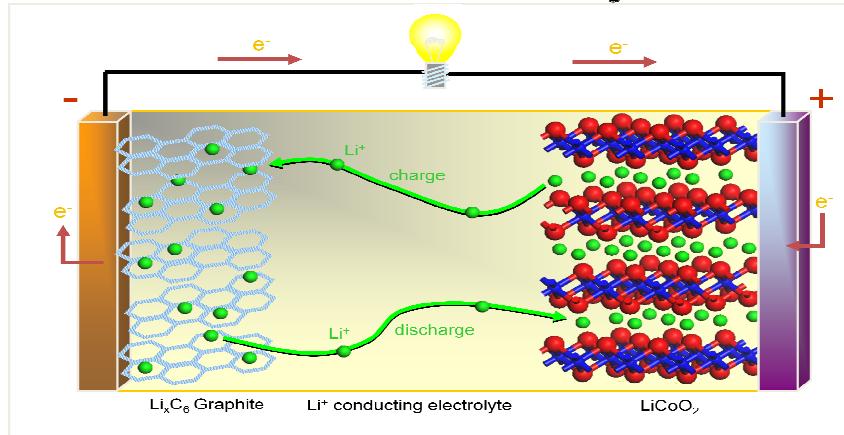
During discharge, lithium ions Li^+ carry the current from the negative to the positive electrode, through the non - aqueous electrolyte and separator diaphragm.

During charging, an external electrical power source (the charging circuit) applies a higher voltage (but of the same polarity) than that produced by the battery, forcing the current to pass in the reverse direction. The lithium ions then migrate from the positive to the negative electrode, where they become embedded in the porous electrode material in a process known as intercalation.

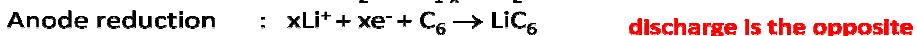
The three participants in the electrochemical reactions in a lithium-ion battery are the anode, cathode, and electrolyte.

Both the anode and cathode are materials into which, and from which, lithium can migrate. During insertion or intercalation lithium moves into the electrode. During the reverse process, extraction or deintercalation, lithium moves back out. When a lithium-based cell is discharging, the lithium is extracted from the anode and inserted into the cathode. When the cell is charging, the reverse occurs.

Li-ion Battery



- Electrode redox reactions on charge:



Useful work can only be extracted if electrons flow through a closed external circuit. The following equations are in units of moles, making it possible to use the coefficient x .

The positive electrode half-reaction (with charging being forwards) is:



The negative electrode half-reaction is:



The overall reaction has its limits. Over discharge supersaturates lithium cobalt oxide, leading to the production of lithium oxide possibly by the following irreversible reaction:



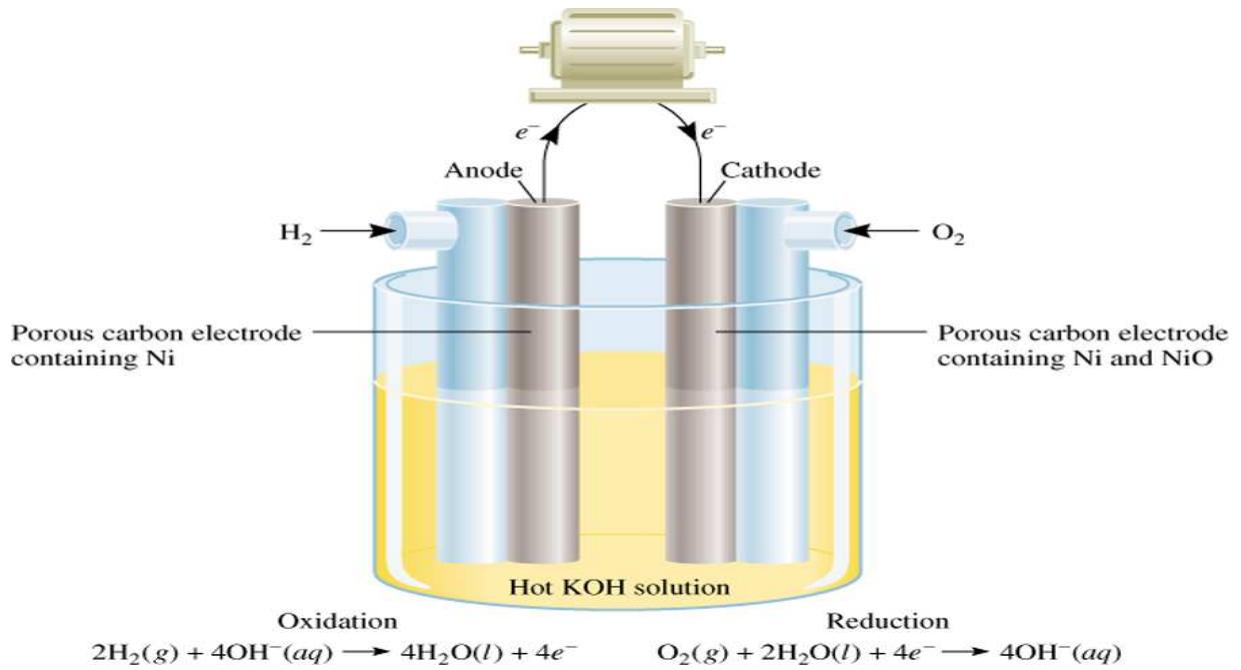
Overcharge up to 5.2 Volts leads to the synthesis of cobalt(IV) oxide, as evidenced by x-ray diffraction



In a lithium-ion battery the lithium ions are transported to and from the cathode or anode, with the transition metal, cobalt (Co), in Li_xCoO_2 being oxidized from Co^{3+} to Co^{4+} during charging, and reduced from Co^{4+} to Co^{3+} during discharge.

3. Fuel Cell: A galvanic cell where there is a continuous supply of reactants.

It consists of two inert porous electrodes made of graphite impregnated with finely divided Pt and 25% KOH solution as electrolyte. Hydrogen gas is bubbled through one inert electrode, acts as anode. Oxygen gas is bubbled through another electrode, acts as cathode. The hydrogen-oxygen fuel cell produces water as a product and hence is an ideal power source for zero-emission vehicles. Hence it is called an eco friendly battery.



Redox Reaction in a Hydrogen- oxygen Fuel Cell

