ELECTROCHEMISTRY

Electrochemical cell

Electrochemistry: Branch of Physical Chemistry which deals with the properties , behavior of electrolytes in solution and inter-conversion of chemical energy (CE) & electrical energy(EE)
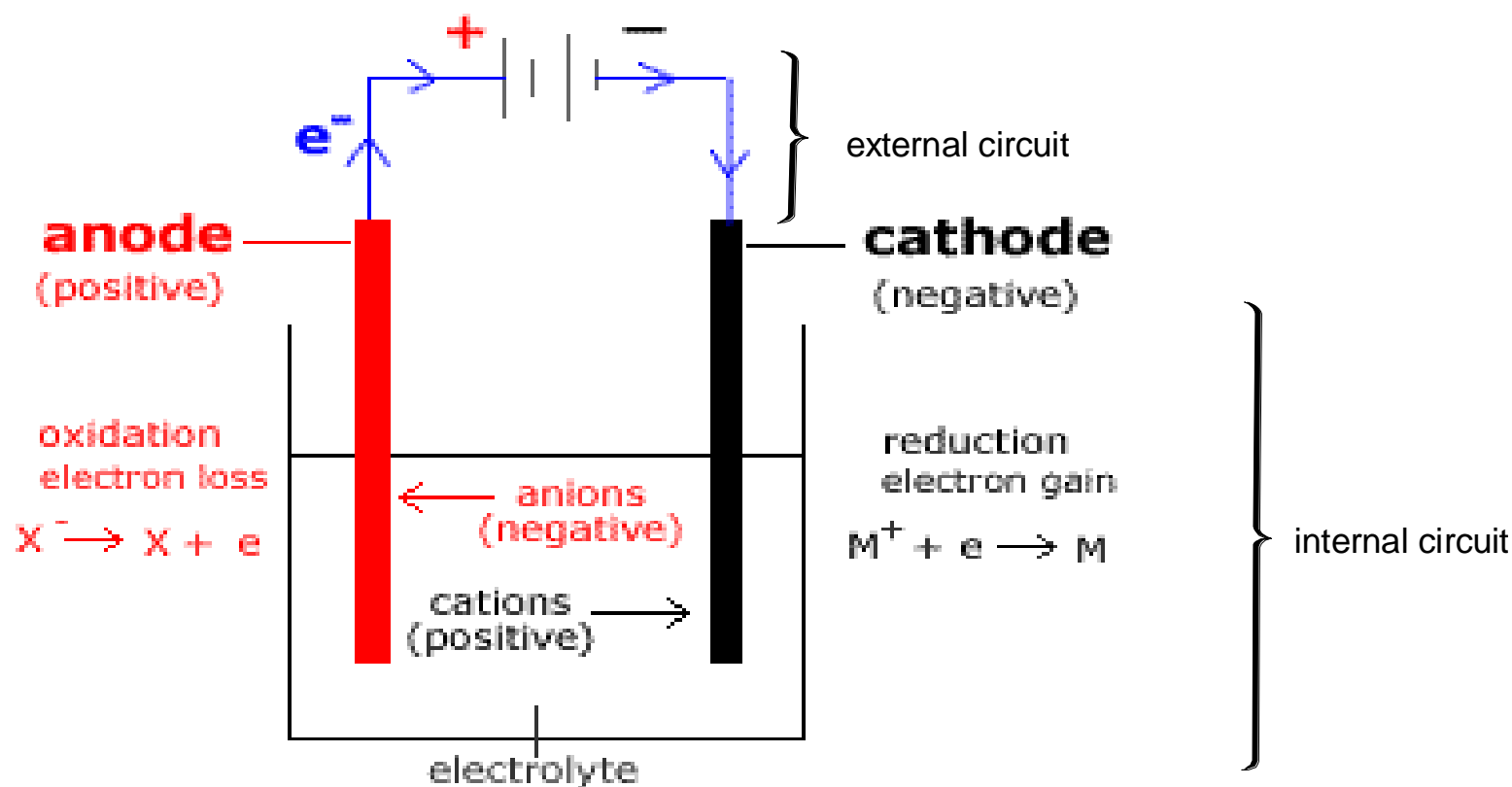
Electrochemical cell - a single arrangement of two electrodes in one or two electrolytes which converts CE into EE or vice versa.
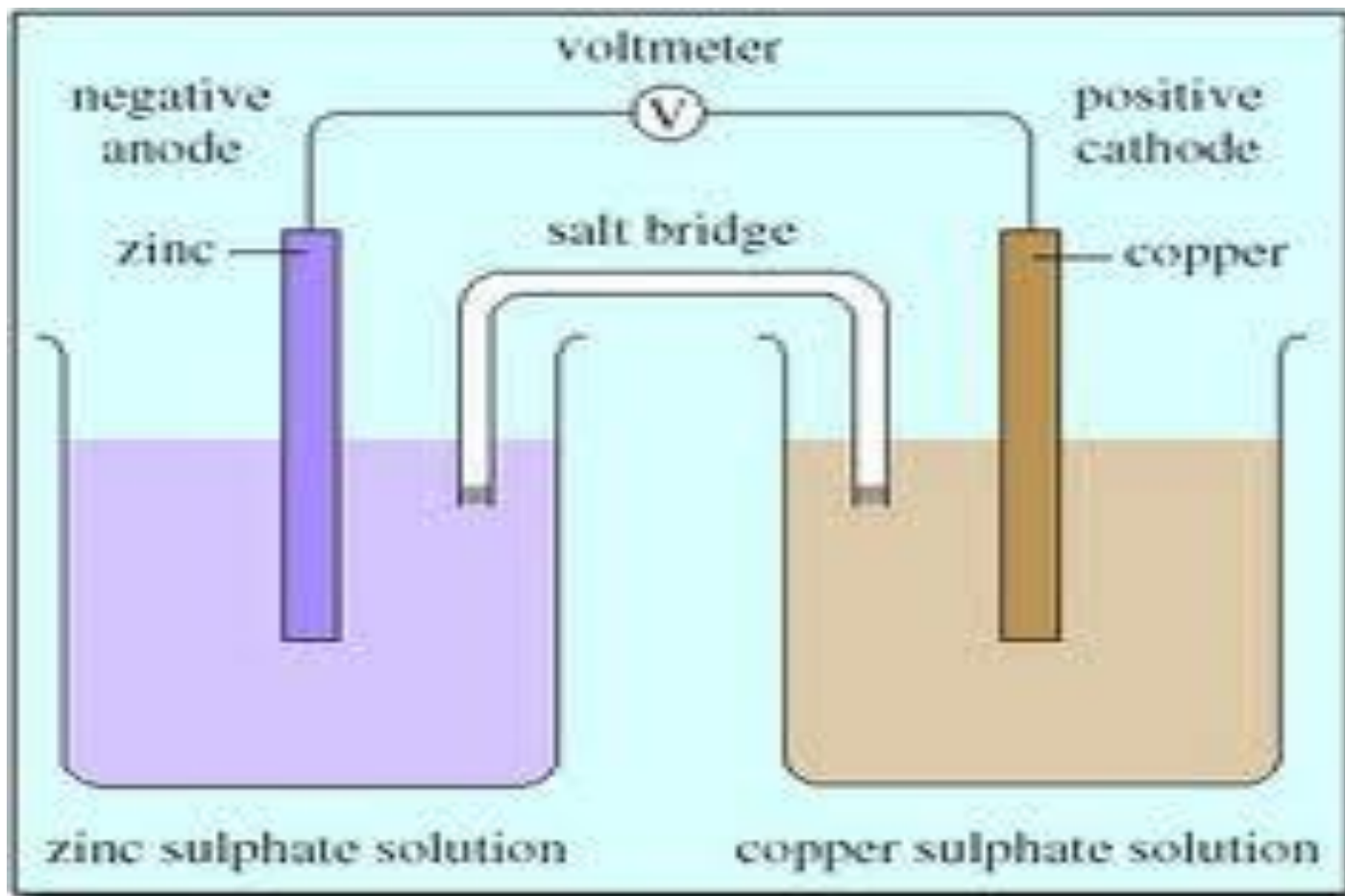
• Classification

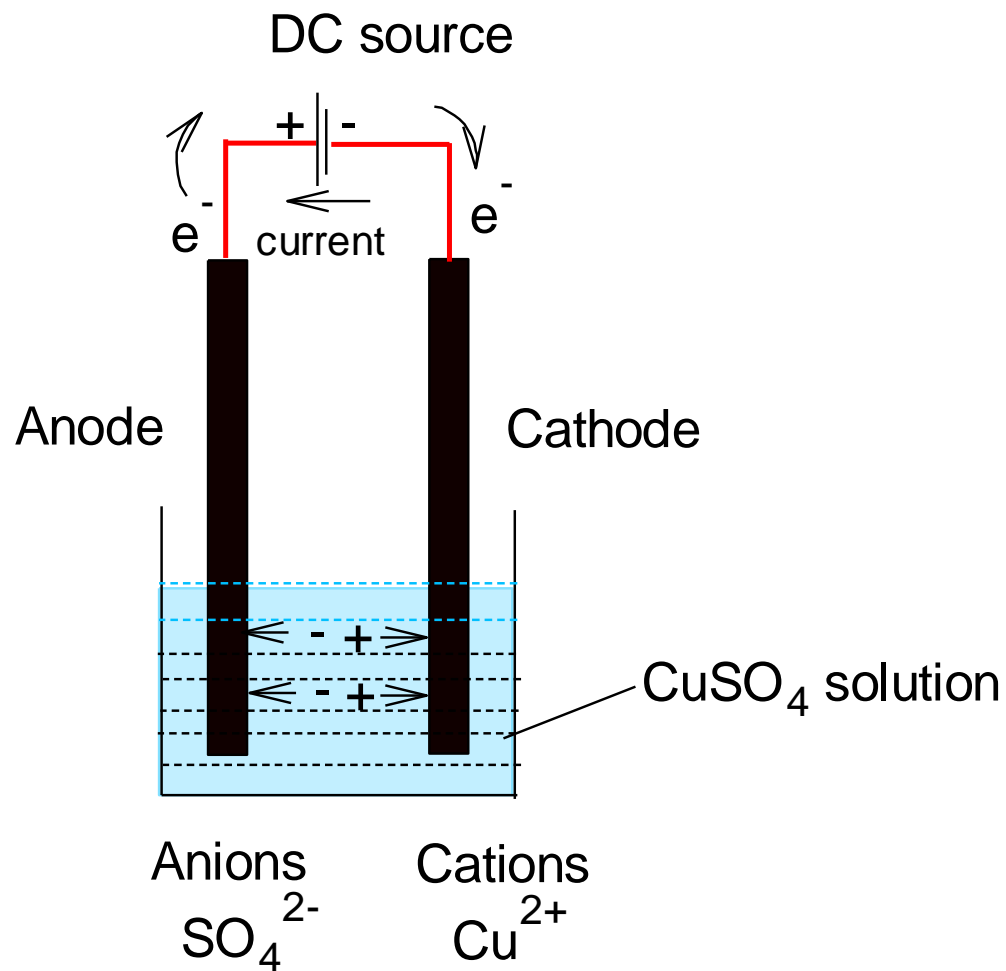   Galvanic Cells
              Electrolytic Cells

Electrochemical Cell

Galvanic Cell- Daniel Cell

Electrolytic Cell

DC source

Anode   Cathode

CuSO$_4$ solution

Anions
SO$_4^{2-}$

Cations
Cu^{2+}

e$^-$ current   e$^-$

Comparisons between Galvanic and Electrolytic Cell

Galvanic Cell

- Cell reaction is spontaneous

- Converts Chemical Energy to Electrical Energy

- Anode is negative terminal and cathode is positive terminal

- Used as portable source of electric energy.

- Eg: Daniel Cell

Electrolytic Cell

- Cell reaction is non spontaneous

- Converts Electrical Energy into Chemical Energy

- Anode is positive terminal and cathode is negative terminal

- Used in Electrolysis apparatus.
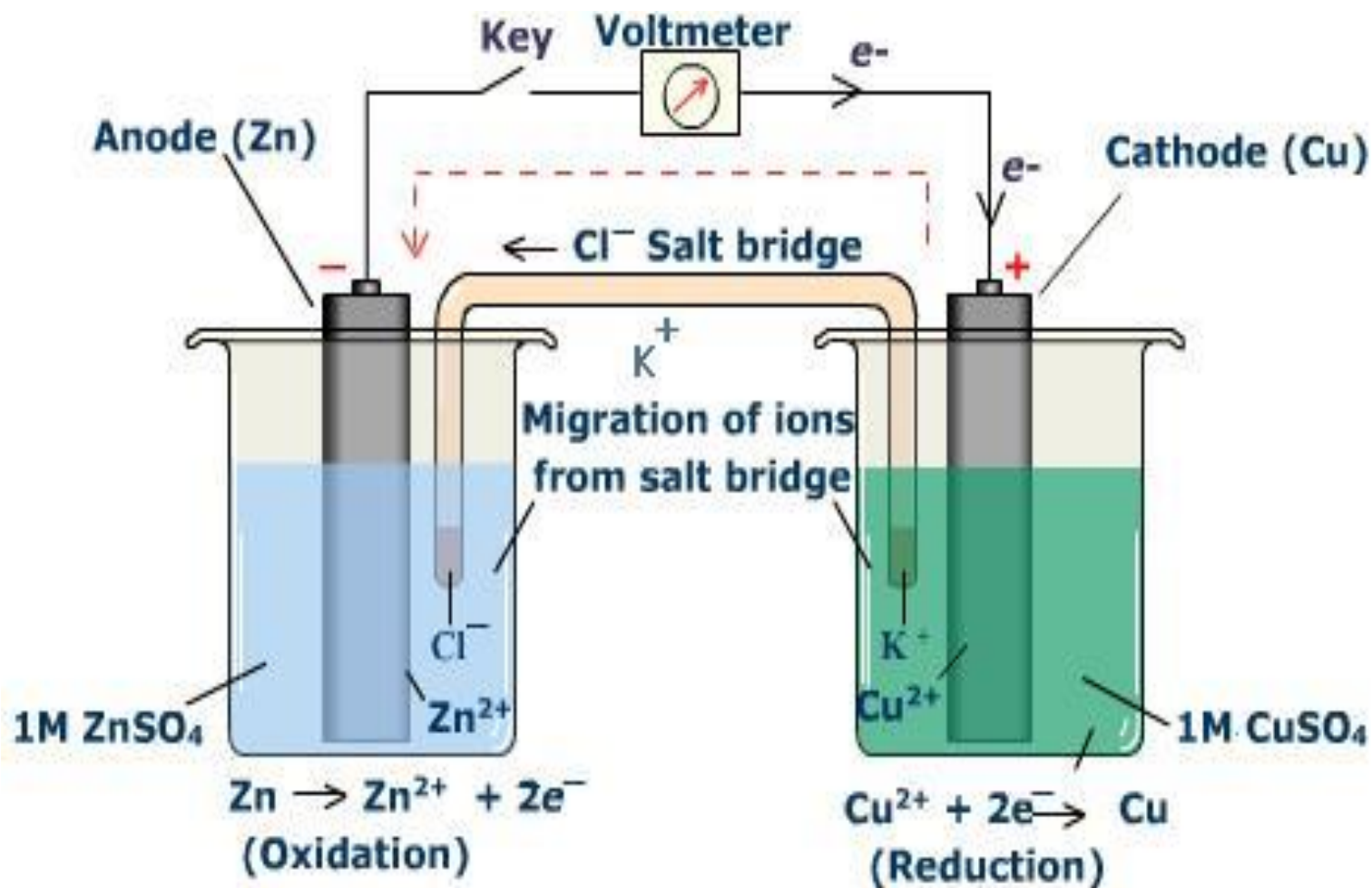
- Eg : Electroplating.

Liquid Junction Potential (LJP)

- Difference between the electric potentials developed in the two solutions across their interface .

- $E_j = \emptyset_{soln, R} - \emptyset_{soln,L}$

  Eg: Contact between:
- ✓ Two different electrolytes ($ZnSO_4$/ $CuSO_4$).
- ✓ Same electrolytes of different concentrations.
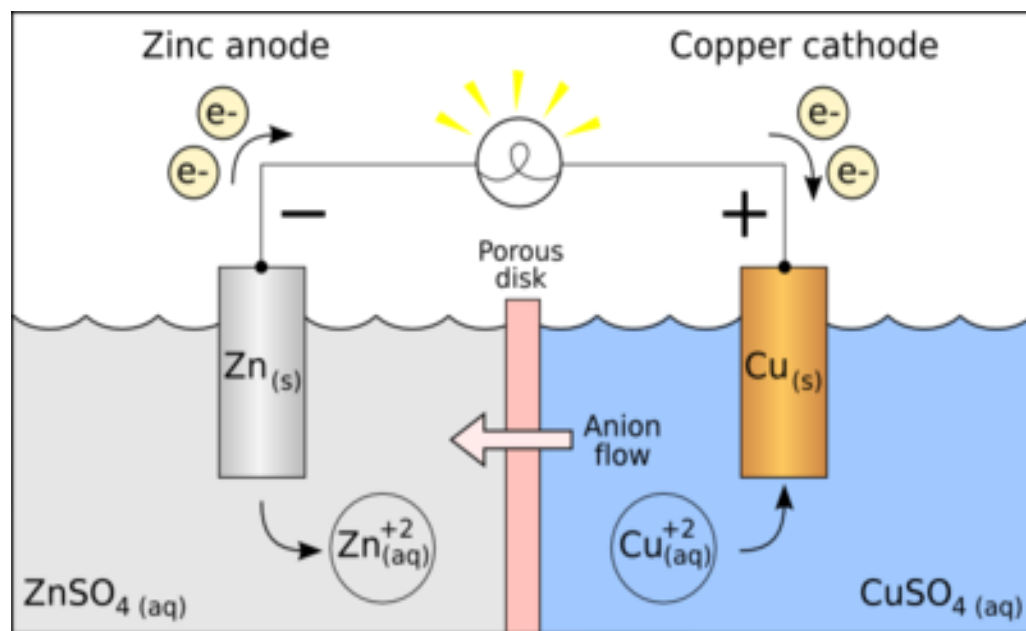
Salt Bridge - Elimination of LJP

Emf of a cell

The difference of potential, which causes a current to flow from the electrode of higher potential to one of lower potential.

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

The emf cannot be measured accurately using a voltmeter :

➢ As a part of the cell current is drawn, thereby causing a change in the emf.

➢ As a part of the emf is used to overcome the internal resistance of the cell.

The potentiometric measurement of emf of a cell: Poggendorff's compensation method

The emf of the cell E_x is proportional to the length AD.
$$E_x \quad \alpha \quad AD$$

The emf of the standard cell E_s is proportional to the length AD^1.
$$E_s \; \alpha \; AD^1$$

$$\frac{E_{x}}{E_s} \; = \; \frac{AD}{AD^1}$$

$$E_x = \frac{AD}{AD^1} \; x \; E_s$$

AB- Potentiometric wire
E_s- Standard cell
Ex- unknown cell
G- Galvanometer
J- Sliding contact.
C-Rh – adjustable resistance
S- Storage battery

Requirements of a standard cell

- It is one which is capable of giving constant and reproducible emf.

- It has a negligible temperature coefficient of the emf.

- The cell reaction should be reversible.

- It should have no liquid junction potential.

Energetics of Cell Reactions

$\Delta G = -nFE$ Joules

$\Delta S = nF(\partial\varepsilon/\partial T)_P$ JK $^{-1}$

$\Delta H = nF[T(\partial\varepsilon/\partial T)_P - E]$ Joules

Problems

1. Emf of Weston Cadmium cell is 1.0183 V at 293 K and 1.0l81 V at 298 K.

   Calculate $\Delta G, \Delta H$ and ΔS of the cell reaction at 298 K.

2. The emf of the cell Cd|CdCl$_2$. 2.5 H$_2$O (saturated) || AgCl(s)| Ag is 0.6753V and 0.6915 V at 298 K and 273 K respectively. Calculate $\Delta G, \Delta H$ and ΔS of the cell reaction at 298 K.

Origin of single electrode potential

Zinc ions moves into solution leaving behind electrons making it electron rich

Copper ions gets deposited as copper leaving behind free negatively charged sulfate ions in solution makes the electrode electron poor

Measurement of electrode potential

- It is impossible to determine the absolute half cell potential.

- We can only measure the difference in potential between two electrodes potentiometrically, by combining them to form a complete cell.

Sign of electrode potential

- When an electrode is coupled with a SHE, if reduction occurs then EP is given a +ve sign

    e.g Copper electrode + SHE

    $Cu^{2+} + 2e^- \rightarrow Cu(s)$ reduction at copper electrode(cathode)

    $H_2(g) \rightarrow 2H^+ + 2e^-$ oxidation at hydrogen elecrode (anode)

    $E^0 = 0.34$ volt

- Similarlly, when an electrode is coupled with a SHE, if oxidation occurs then EP is given a -ve sign

    e.g . Zinc electrode + SHE

    $Zn (s) \rightarrow Zn^{2+}(aq) + 2e^-$ (oxidation)

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

    $E^0 = - 0.76$ volt

Nernst Equation

It is a quantitative relationship between electrode potential and concentration of the electrolyte species.

$$E = E^o - 0.0592/n \log 1/[M^{n+}] \quad \text{at } 298K$$

From Nernst equation, it is clear that;

- If concentration of solution (M^{n+}) is increased, the electrode potential increases and vice versa.

- If temperature is increased, the electrode potential increases and vice versa.

Electrochemistry

Problems

1. A galvanic cell consists of copper plate immersed in 10 M solution of $CuSO_4$ and iron plate immersed in 1M $FeSO_4$ at 298K.
If $E^0_{cell} = 0.78$ V, write the cell reaction and calculate E.M.F. of the cell.

2. Calculate E.M.F. of the zinc – silver cell at 25˚C when $[Zn^{2+}] = 1.0$ M and $[Ag^+] = 10$ M (E^0_{cell}=1.56V at 25˚C). Write the cell representation and cell reaction.

3. The emf of the cell
Cd/ $CdCl_2$.2.5 H_2O(sat'd) // AgCl (s) / Ag
is 0.6753 V and 0.6915 V at 298 K and 273 K respectively. Calculate ΔH , ΔS and ΔG at 298 K.

Calomel electrode
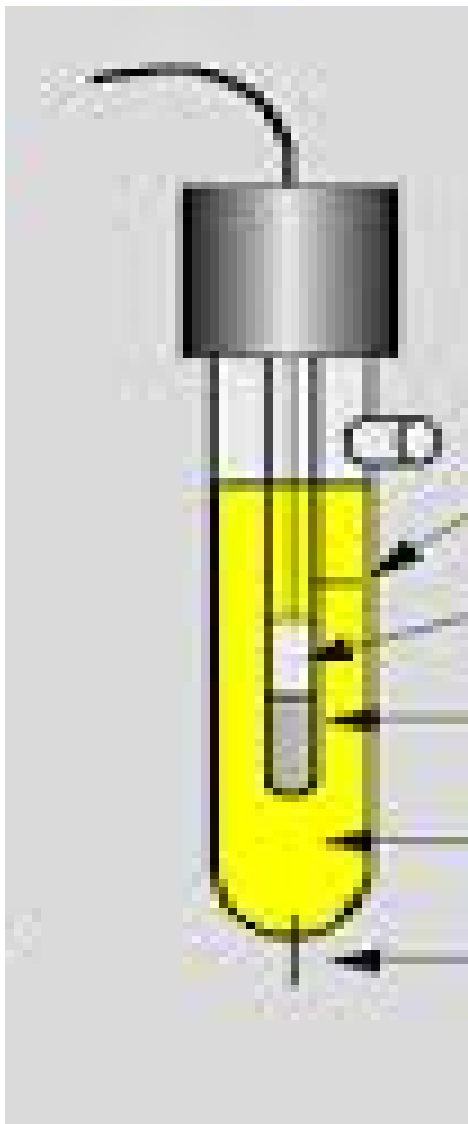
- It consists of a tube, in the bottom of which is a layer of mercury, over which is placed a paste of mercury and mercury chloride.

- The remaining portion of the cell is filled with a solution of normal or decinormal or saturated solution of KCl.

- A platinum wire sealed at its end fixed into the main tube dipping into the mercury layer is used for making electrical contact.

External Contact wire

Salt bridge connector

Glass envelope

$Hg+ Hg_2Cl_2$

Saturated KCl

Platinum wire
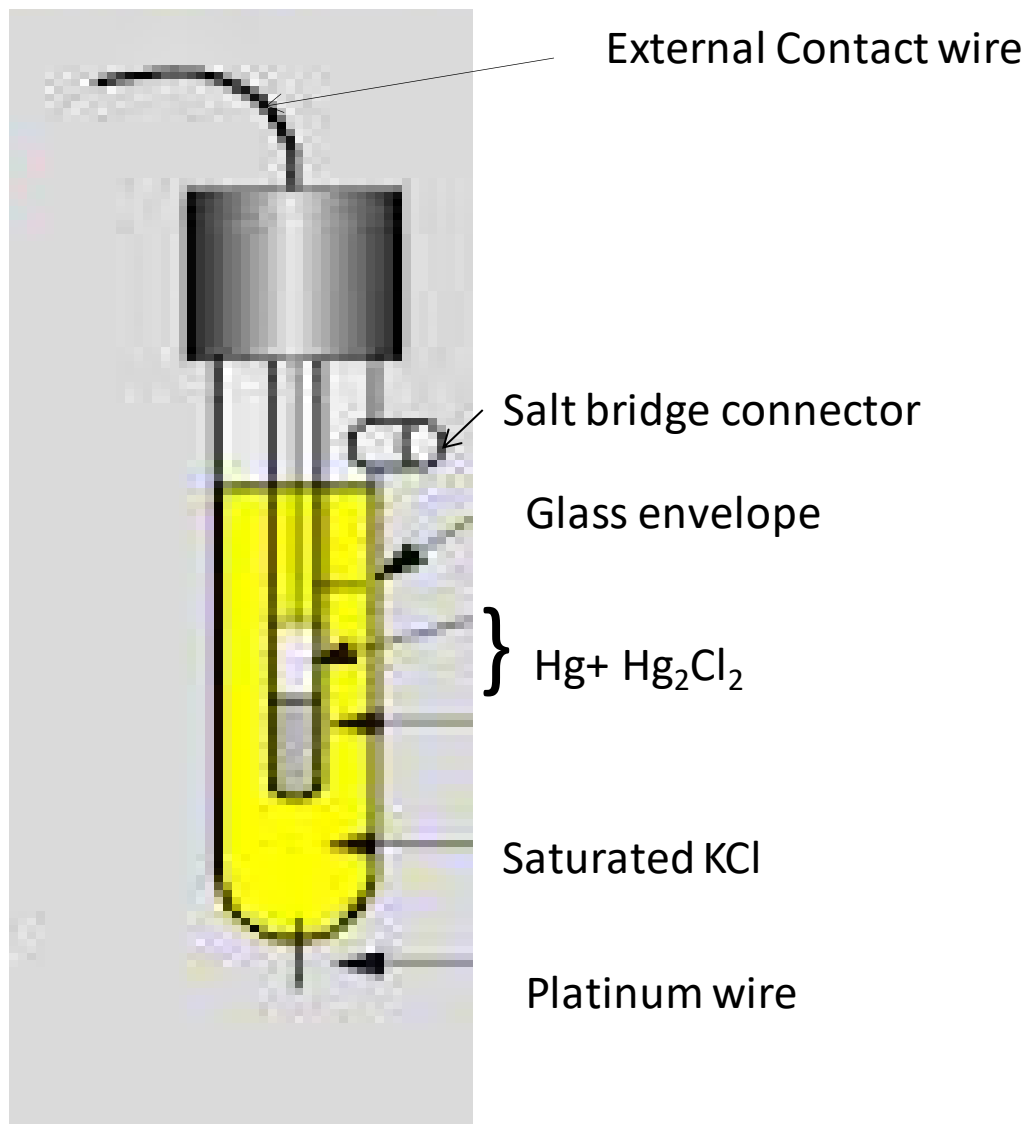
Advantages

- It is very simple to construct.
- It can be used for a long time without much attention.
- Electrode potential is stable over a long period.
- It has low temperature coefficient of emf.
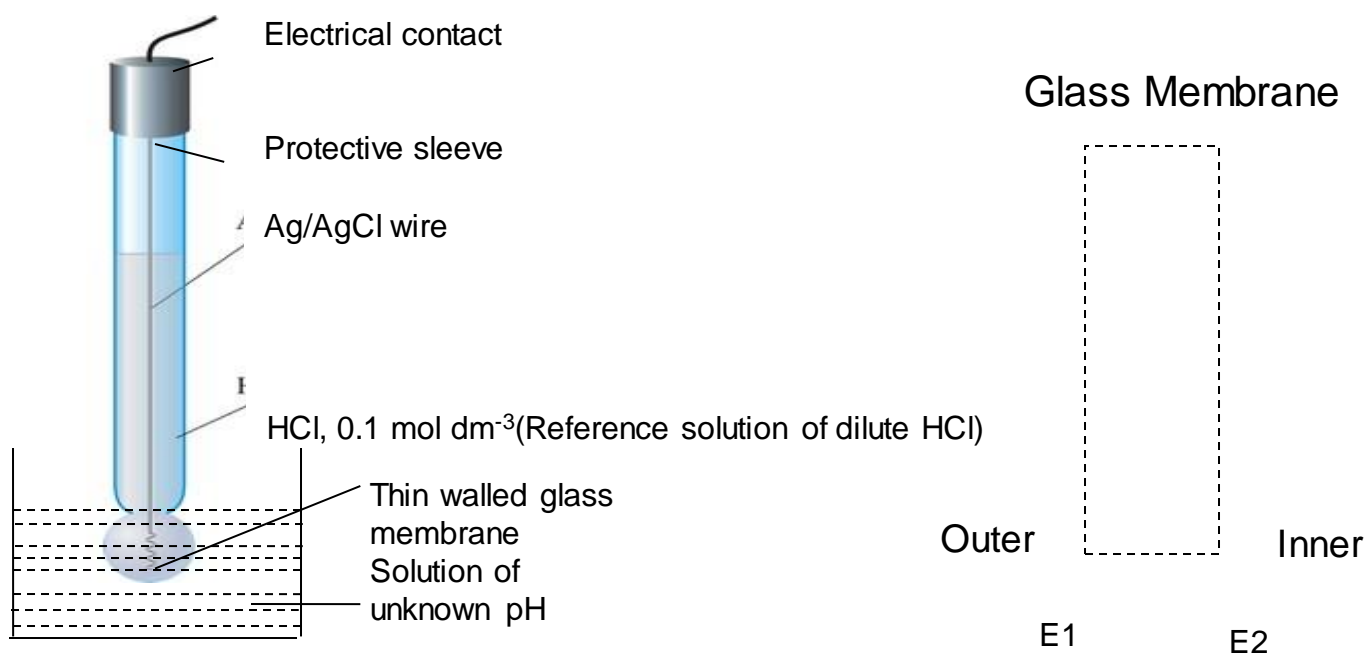- It is less prone to contamination.

Disadvantages

- Calomel electrodes should not be used above 50°C .
- Calomel electrode should be used with proper precaution as mercury compounds are toxic.

Ion Selective Electrode

- The electrode which is sensitive to a specific ion present in an electrolyte whose potential depends upon the activity of specific ion in the electrolyte is called ion selective electrode.

- The magnitude of potential of this electrode is an indicator of the activity of the specific ion in the electrolyte. Example for this type of electrode is glass electrode.

Electrochemistry

Glass electrode

Electrical contact

Protective sleeve

Ag/AgCl wire

HCl, 0.1 mol dm^{-3}(Reference solution of dilute HCl)

Thin walled glass membrane
Solution of unknown pH

Glass Membrane

Outer

Inner

E1

E2

Electrochemistry

Electrode Potential of glass electrode.

The overall potential of the glass electrode is given by:

$$E_g = E_b + E_{ref.} + E_{asy.}$$

It has three components:

➢ *The boundary potential E_b,*

➢ *Internal reference electrode potential $E_{ref.}$*

➢ *Asymetric potential E_{asy}*

$E_b = E_1-E_2$ _____ (1)

Where E_b is the boundary potential

E_1 = potential developed at the interface between the exterior of the glass and the analyte solution

E_2 = Potential developed at the interface between the internal solution and the interior of the glass. The boundary potential is related to the concentration of hydrogen ion in each of the solution by the Nernst-like equation.

$E_b = E_1 - E_2 = 0.0592 \log C_l / C_2$ _____ (2)

For a glass pH electrode the hydrogen ion concentration of the internal solution is held constant. So eqn. (2) becomes

$E_b = K + 0.0592 \log C_1$ _____(3)   (Recall pH= -log [H^+]

Asymmetry potential include the following.

(i) Differing conditions of strain in the two glass surfaces during manufacture
(ii) Mechanical abrasion on the on the outer surface during use
(iii) Chemical etching of the outer surface during use.

The asymmetry potential changes slowly with time.

The glass electrode potential can be written in the equation form as

$E_G = E_b + E_{Ag/AgCl} + E_{asym}$ _____ (4)

Substitution of eqn – (3) for E_b, gives

$E_G = K + 0.0592 \log C_1 + E_{Ag/AgCl} + E_{asym}$

$\quad = K - 0.0592 \log pH + E_{Ag/AgCl} + E_{asym}$ ____(5)

$E_G = E^o_G - 0.0592 \; pH$ _____(6)

where $E^o_G = K + E_{Ag/AgCl} + E_{asym.}$ a combination of three constant terms

= constant

To measure the hydrogen ion concentration of the test solution, the glass electrode (indicator electrode) must be combined with an external reference electrode, which is required for all kinds of ion-selective electrode determinations.

Advantages of glass electrode

1. It can be used without interference in solutions containing strong oxidants, strong reductants, proteins, viscos fluids and gases.

2. It can be used for solutions having pH values 2 to 10. With some special glass (by incorporation of Al_2O_3 or B_2O_3) measurements can be extended to pH values up to 12.

3. It is immune to poisoning and is simple to operate

4. The equilibrium is reached quickly & the response is rapid

5. It can be used for very small quantities of the solutions

6. The glass electrode is much more convenient to handle than the inconvenient hydrogen gas electrode.

Disadvantages of glass electrode

1. The bulb is very fragile and has to be used with great care.

2. In the presence of alkali ions, the glass surface becomes responsive to both hydrogen and alkali ions. Measured pH values are low.

3. In highly acidic solutions measured pH values are high.

4. When not in use, the electrode should be stored in an aqueous solution.

5. The commercial verson is moderately expensive

Applications of glass electrode

Determination of pH:
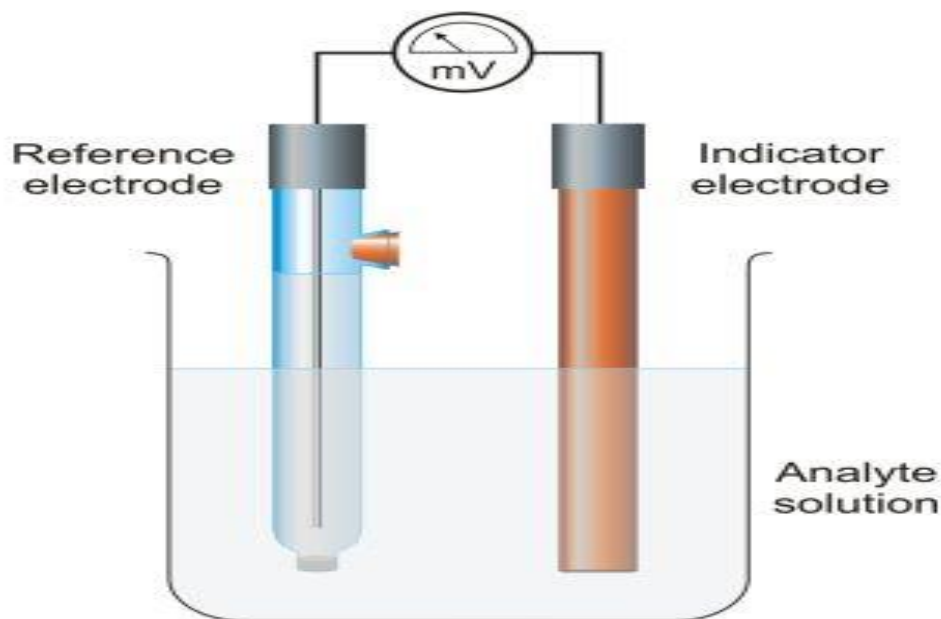
Cell: SCE / Test solution / GE

Problem

The cell SCE II (0.1M) HCl I AgCl(s), Ag

gave emf of 0.24 V and 0.26 V with buffer having pH value 2.8 and unknown pH value respectively. Calculate the pH value of unknown buffer solution. Given E_{SCE}= 0.2422 V

Summary

- It is very important to know the types of electrochemical cells, their representation and working as electrochemistry has a vital role in electro refining, battery technology, corrosion control and metal finishing.

- A brief description about the origin of single electrode potential, its measurements and sign convention also discussed.

- Although it is impossible to measure the absolute electrode potential, we can measure the difference in potential which is a key concept in electrochemistry.

- The Nernst equation is derived for the electrode as well as to the cell systems and its significance highlighted.

- Construction and working of calomel and glass electrodes described to know the basic differences between reference and indicator electrodes.

- Basic concepts regarding concentration cell, its construction and working are discussed.

Self -Test

1. Distinguish between:
   a) electrolytic & galvanic cell
   b) anode & cathode in an electrochemical cell

2. Give the cell representation, half cell reactions & net cell reactions of Daniel cell.

3. Describe the origin of LJP. How can it be minimized?

4. Justify the statement: KCl is preferred to NaCl in the preparation of salt bridge.

5. Describe the construction and working of glass electrode

References

1. P.C. Jain & M. Jain, *Engineering Chemistry*, Edn.15, Dhanpat Rai Publishing Company, New Delhi, **2005**.

2. P.W. Atkins & J.D. Paul, *Physical Chemistry*, Edn.8, Oxford University Press, Oxford, **2006**

BATTERY TECHNOLOGY→Contents

- Introduction to batteries

- Basic concepts

- Battery characteristics

- Classification, Dry cell, Li-CuS cell, Lead-acid, Nicad- & lithium ion batteries

- Fuel cells, Construction & working of alkaline FC, proton exchange membrane FC & direct methanol FC

Learning objectives

- Demonstrate an understanding of the meaning of the terms cell, battery, charging, recharging, separator, fuel cell.

- Describe construction & working of some battery systems & fuel cells.

- Distinguish between primary & secondary battery types.

- Explain the effect of overcharging lead acid battery

- Make accurate qualitative statements about battery systems

- Identify the advantages & disadvantages of typical battery systems.

Terms

- Cell
- Battery
- Charging
- Discharging
- Separator
- Fuel cell
- Cycle life
- Shelf
- Design life

- Voltage
- Current
- Capacity
- Electricity storage density
- Power

Capacity: The capacity is the charge or the amount of electricity that may be obtained from the battery and is given in ampere hours (Ah).

$$\text{Capacity} = I \times t$$

Where I = Current

t = time

Electricity storage density: Electrical storage density is the amount of electricity per unit weight which the storer can hold, it's the capacity per unit weight of the battery.

Power (Watts): The electric power P is equal to the energy consumption E divided by the consumption time t:

P is the electric power in watt (W).

E is the energy consumption in joule (J).

t is the time in seconds (s).

Power (Watts) = EI, Where E = Voltage, I = Current

Shelf life: Time an inactive battery can be stored before it becomes unusable i.e,the length of time a battery can remain without losing its energy capacity

Design life: Elapsed time before a battery becomes unusable whether it is in active use or inactive.

Classification & comparison of commercial cells – Differences & similarities

Primary Batteries	Secondary Batteries
1.Cell reaction is irreversible	Cell reaction is reversible
2. Must be discarded after its active elements have been consumed	May be recharged a number of times from an external d.c. source during its useful life
3. Have relatively short shelf life	Have very long shelf life
4. Function only as galvanic cells	Function as galvanic cells during discharge as & as electrolytic cells during charging process.
5. Cannot be used as energy storage devices	Can be used as energy storage devices (e.g. solar/ thermal energy converted to electrical energy)
6. Cannot be recharged	Can be recharged.
e.g. Dry cell, Li-MnO$_2$ battery	e.g.Lead acid battery, Ni-cd battery

Basic requirements of cells

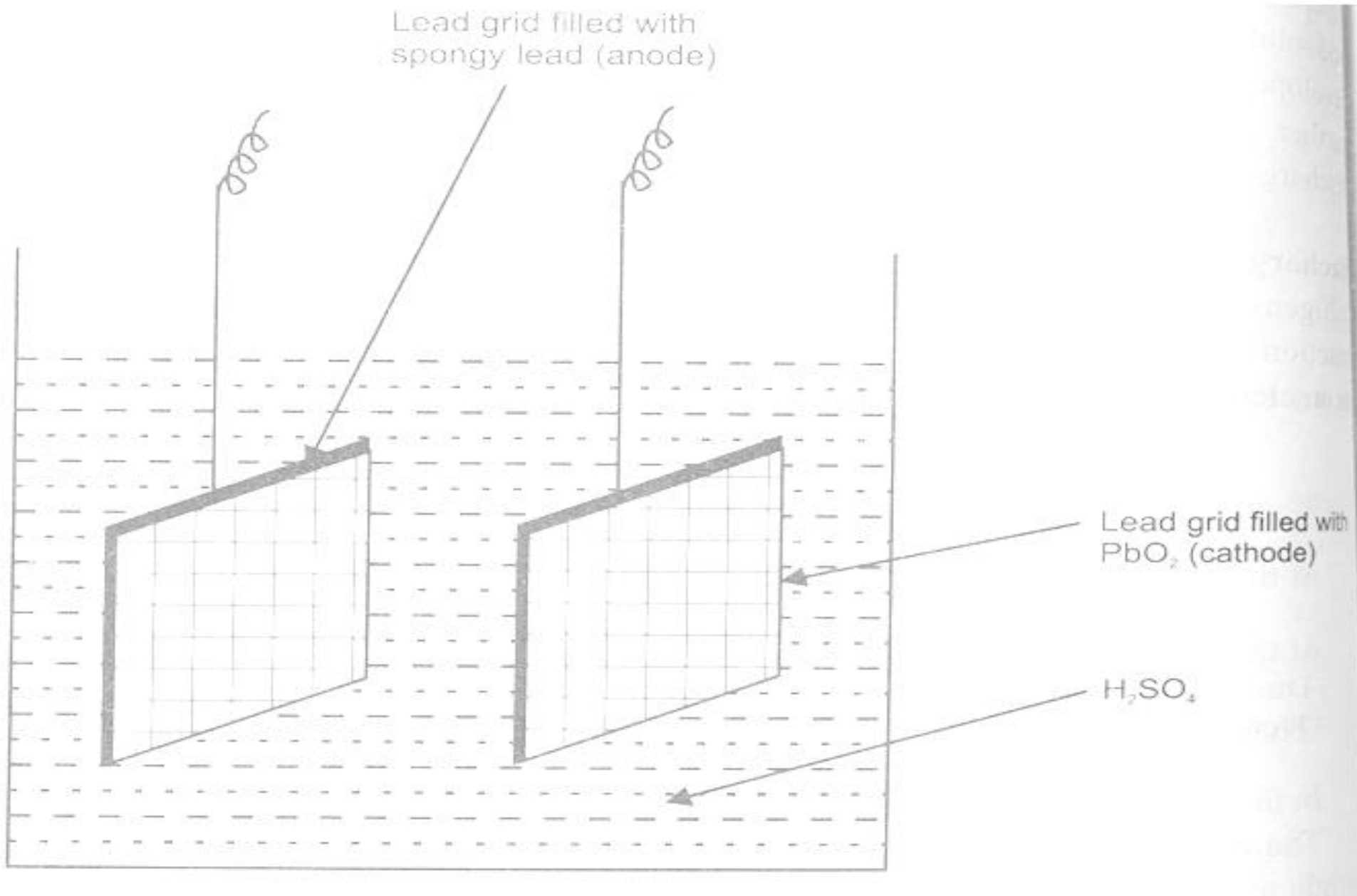| Primary cell	Secondary cell
• Compact, light weight & fabricated easily • High energy density & constant voltage • Benign environmental properties • Longer shelf life & discharge period • Leak proof containers & variety of design options. • Economically priced	• Long shelf-life in both charged & discharged conditions • Longer cycle life & design life • High power to weight ratio • Short time for recharge. • High voltage & high energy density

Lead Storage Battery

Lead grid filled with spongy lead (anode)

Lead grid filled with PbO_2 (cathode)

H_2SO_4

Effect of overcharging

- $2H_2O$ (l) + electrical energy $\rightarrow$ $2H_2$ (g) + O_2(g)

Consequences:

(i)Reduce the acid level and damage the exposed

electrode grids

(ii)Dangerous high-pressure build-up that can lead to a

serious risk of explosion.

- Modern maintenance-free batteries

- **Modern maintenance-free batteries:**

- without a gas – release vent. Gassing is controlled by using

- **1**. Pb-Ca (0.1 %) as the anode which inhibits the electrolysis of water.

- **2**. a catalyst (e.g. a mixture of 98% ceria (cerium oxide) & 2% platinum) that combines the hydrogen & oxygen produced during discharge back into water

Lead Storage Battery

Advantages	Disadvantages
• highly efficient • good service for several years • low internal self – discharge • provide a large current	• Sulfation • low energy storage to weight ratio • CP decreases with decrease in conc. of sulfuric acid • not efficient at LT • Overcharging may damage the exposed electrodes & may also lead to explosion in extreme cases • Sulfuric acid is highly corrosive liquid • Lead is toxic & hence environmental & health problems • corrosion of the lead grid at the lead dioxide electrode

Nickel Cadmium Cell
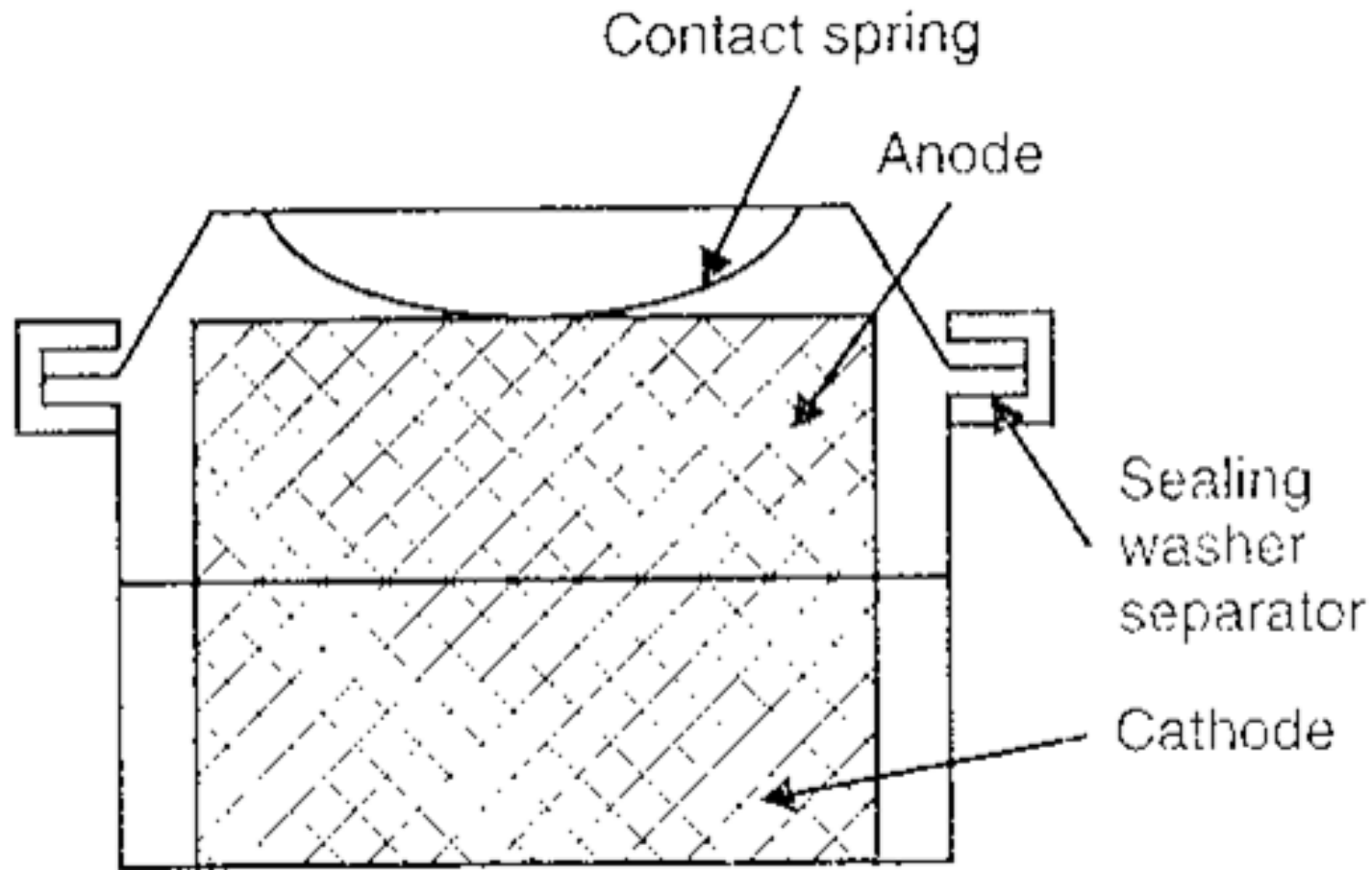
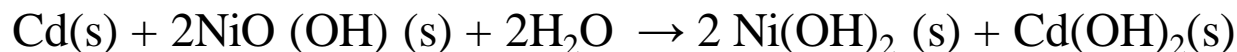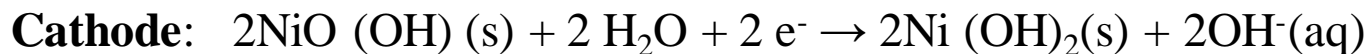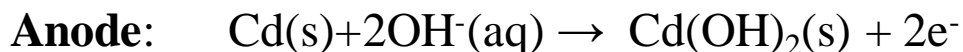# Nickel Cadmium Cell

Advantages

- Long cycle life
- Constant voltage
- Long shelf life
- No gassing
- Long design life
- Good performance at LT
- Produce large instantaneous currents
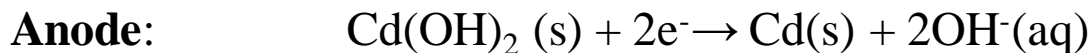
Disadvantages

- Environmental pollution hazard
- Increased weight
- High overall capital cost
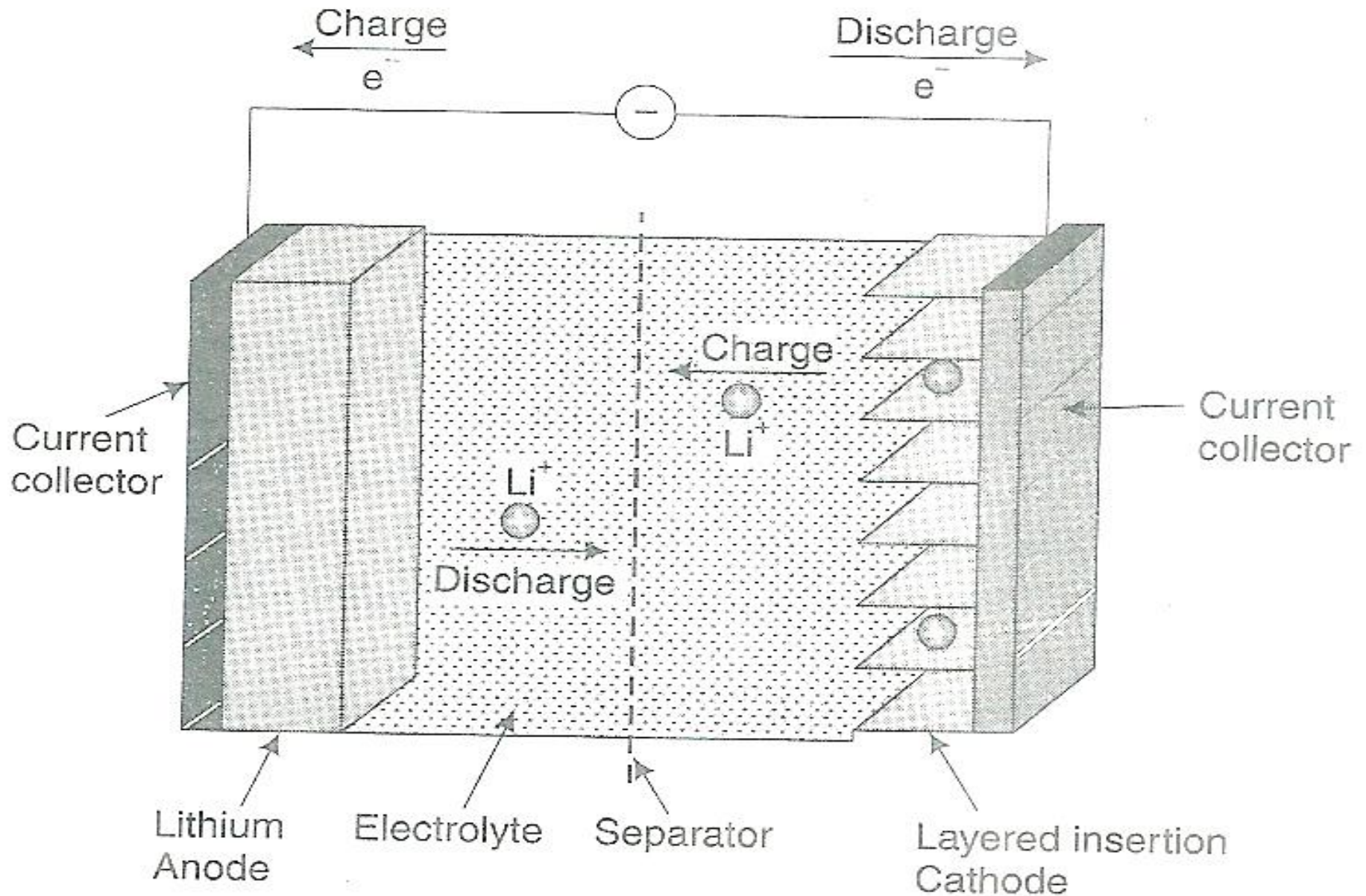- KOH is a corrosive hazardous chemical

Working:

Discharging

Anode: $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$

Cathode: $2NiO(OH)(s) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$

_____

     $Cd(s) + 2NiO(OH)(s) + 2H_2O \rightarrow 2Ni(OH)_2(s) + Cd(OH)_2(s)$

_____

Charging reactions:

Anode: $Cd(OH)_2(s) + 2e^- \rightarrow Cd(s) + 2OH^-(aq)$

Cathode: $2Ni(OH)_2(s) + 2OH^-(aq) \rightarrow 2NiO(OH)(s) + 2H_2O + 2e^-$

_____

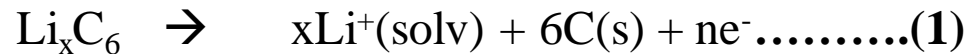**Overall reaction:** $2Ni(OH)_2(s) + Cd(OH)_2(s) \rightarrow 2NiO(OH)(s) + Cd(s) + 2H_2O(l)$

Lithium ion cells

Lithium metal cannot be used safely in secondary batteries. Hence, various lithium compounds have been made, which are used in rechargeable batteries, commonly known as Lithium ion cells. In these type of batteries, lithiated metal oxide such as $LiCoO_2$, LiV_2O_5, & $LiMn_2O_4$ are inserted into the cathode which consists of a layered graphite crystal. The electrolyte is normally $LiPF_6$, but $LiBF_4$ can also be used as $LiPF_6$ is not corrosion resistant.
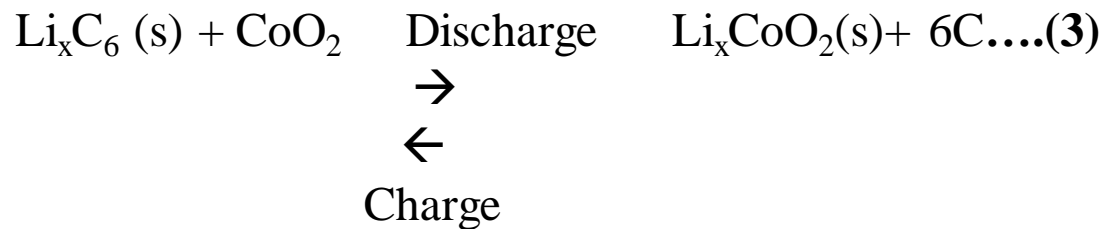
At anode:-

$$Li_xC_6 \rightarrow xLi^+(solv) + 6C(s) + ne^- \ldots\ldots(1)$$

At cathode:-

$$CoO_2(s) + xLi^+(solv) + ne^- \rightarrow Li_xCoO_2(s) \ldots (2)$$

Net cell reaction:-

$$Li_xC_6(s) + CoO_2 \quad \text{Discharge} \quad Li_xCoO_2(s) + 6C\ldots(3)$$

$$\rightarrow$$
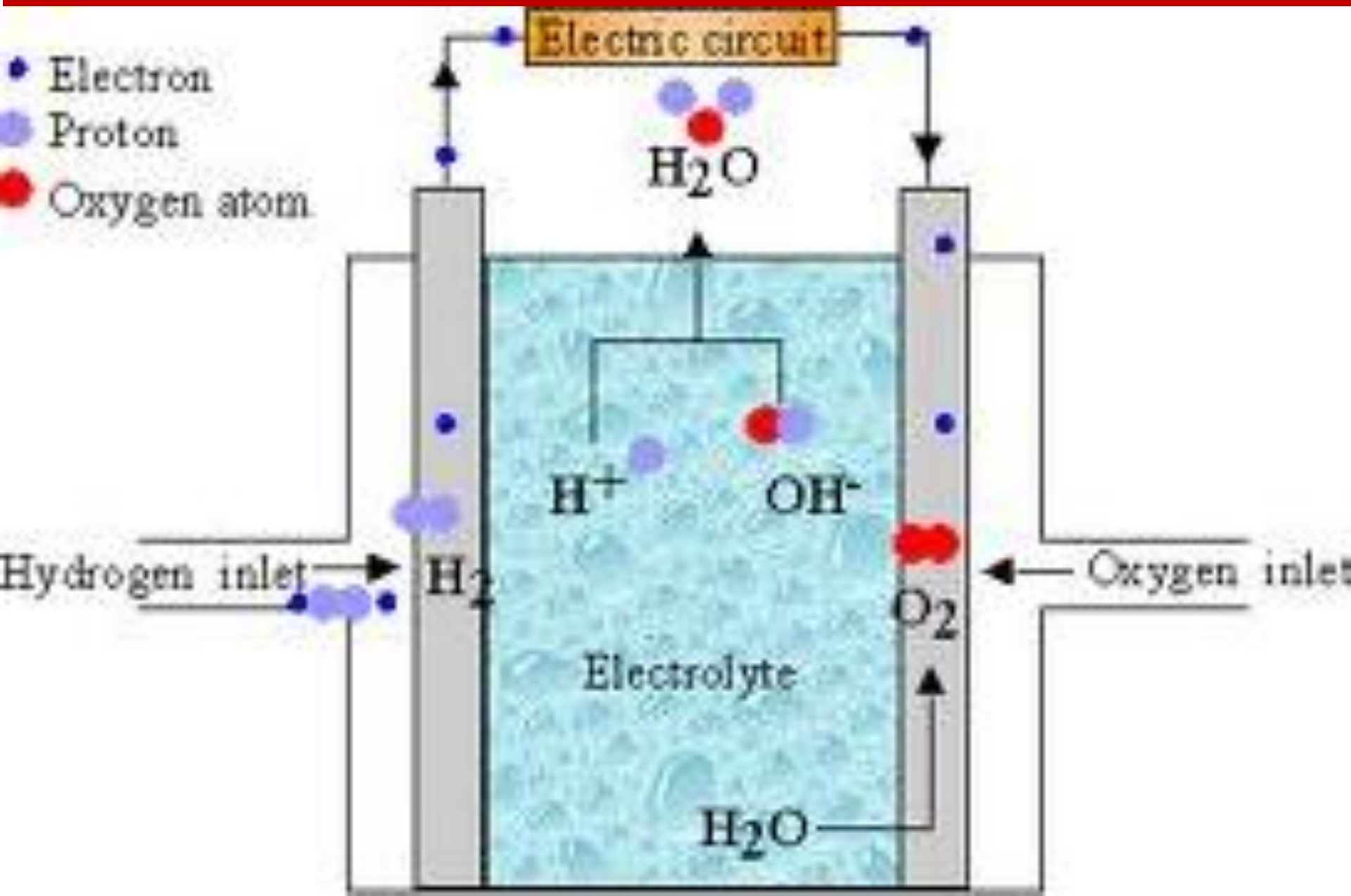
$$\leftarrow$$

Charge

Lithium - ion Cell

Advantages

- Designed to overcome the safety problems
- Long cycle life
- Small, light & provide high energy density
- Can be operated in a wide temperature range
- High average voltage

Disadvantages

- Poor charge retention
- Self discharge rate is about 10% per month
- High cost

Fuel cells

:

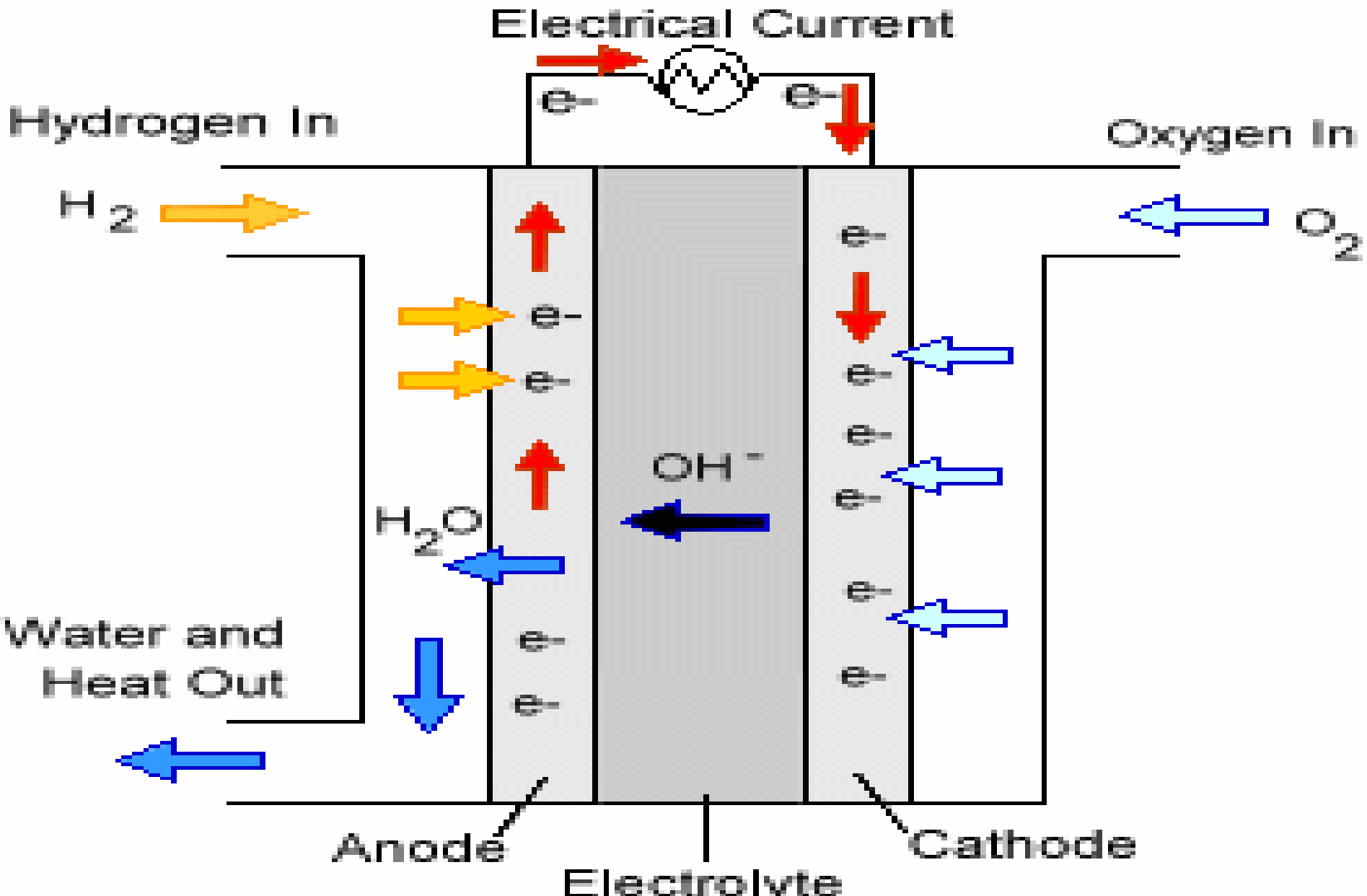*Fuel/ electrode/electrolyte/electrode/oxidant*.

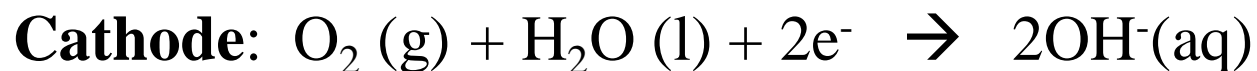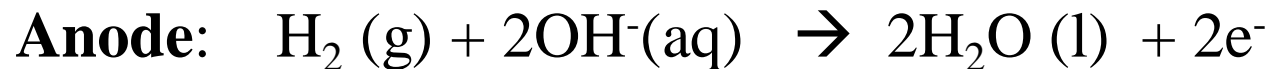**Anode**: Fuel + oxygen $\rightarrow$ Oxidation products+

ne-

Cathode: Oxidant + ne$^-$ $\rightarrow$ Reduction products

- **Advantages:**

1. High fuel to electricity conversion efficiency of 70-75 % while a thermal power plant converts 35-40% chemical energy of coal into electrical energy.

2. Fuel cell products do not cause pollution problems such as noise pollution, chemical pollution & thermal pollution normally associated with conversional power plants.

3. Fuel cell power plants can be located near the point of use electricity such as on an urban location, rather than at a remote place. So transmission & distribution loses (~30%) could be avoided.

4. A fuel cell will produce a steady electric current as long as fresh reactants are available.

Alkaline fuel cell

Anode: $H_2 (g) + 2OH^-(aq) \rightarrow 2H_2O (l) + 2e^-$

Cathode: $O_2 (g) + H_2O (l) + 2e^- \rightarrow 2OH^-(aq)$

Overall: $H_2 + O_2 \rightarrow H_2O (l)$

The cell operates at about 80 ^{0}C & the normal voltage is 1.10 V.

Alkaline fuel cell
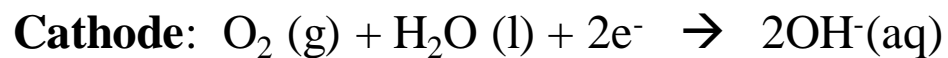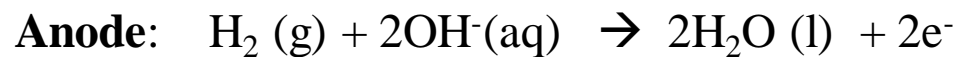
Advantages	Disadvantages
❑ Active O_2 electrode kinetics ❑ Flexible to a wide range of electro-catalysts	1. Electrolyte sensitive to CO_2 2. Reformer with a highly effective CO & CO_2 removal system

Working:-

Anode: H_2 (g) + 2OH$^-$(aq) → 2H$_2$O (l) + 2e$^-$

Cathode: O_2 (g) + H$_2$O (l) + 2e$^-$ → 2OH$^-$(aq)

Overall: H_2+ O_2 → H$_2$O (l)

The cell operates at about 80 ^{0}C & the normal voltage is 1.10 V.
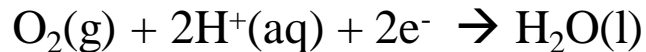
Proton exchange membrane fuel cell
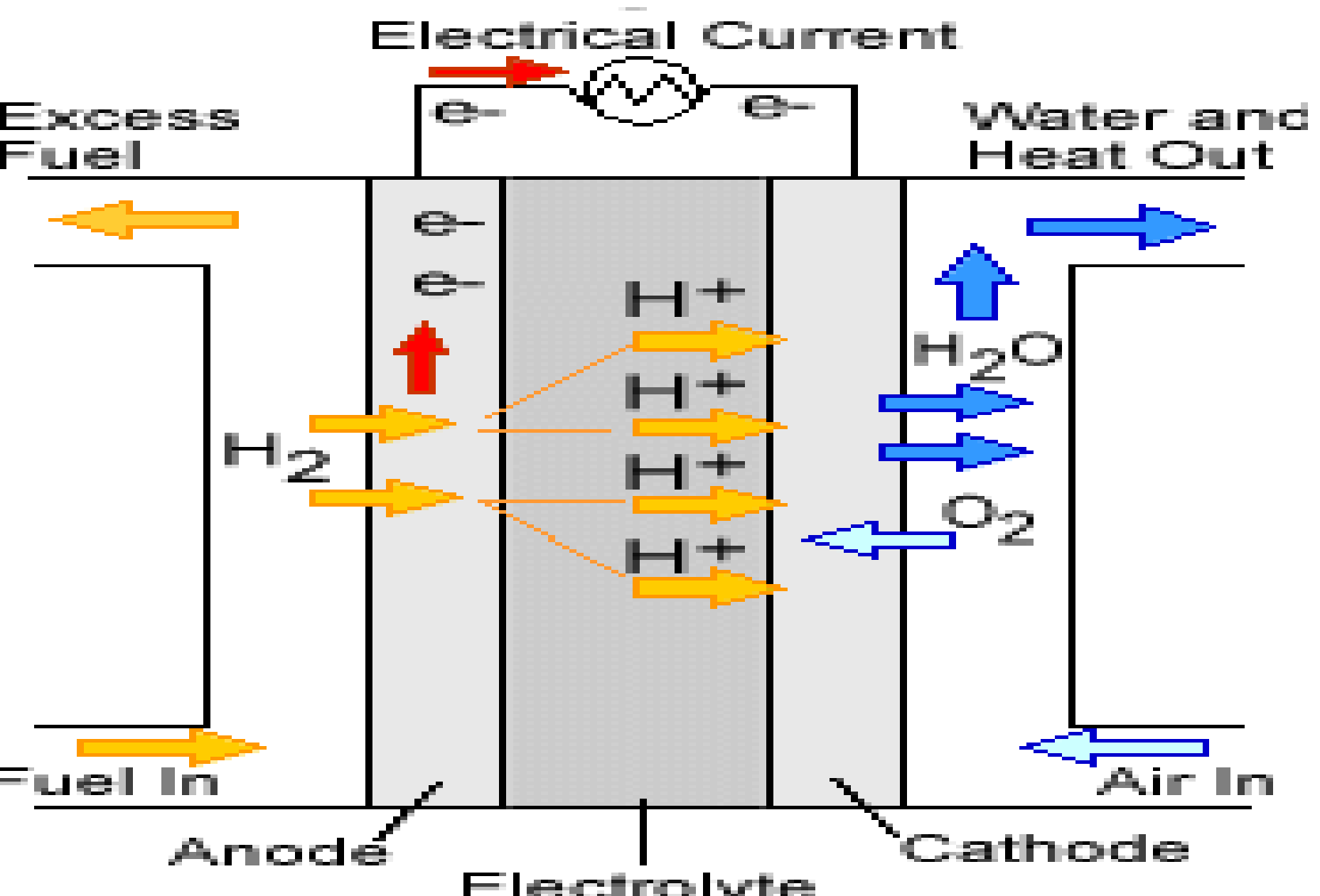
- **Construction:**
- **Electrodes:** Porous carbon containing a platinum catalyst
- **Fuel:** Hydrogen
- **Oxidant:** Oxygen
- **Electrolyte:** Solid polymer
- Operating Temperature: 40-80 °C
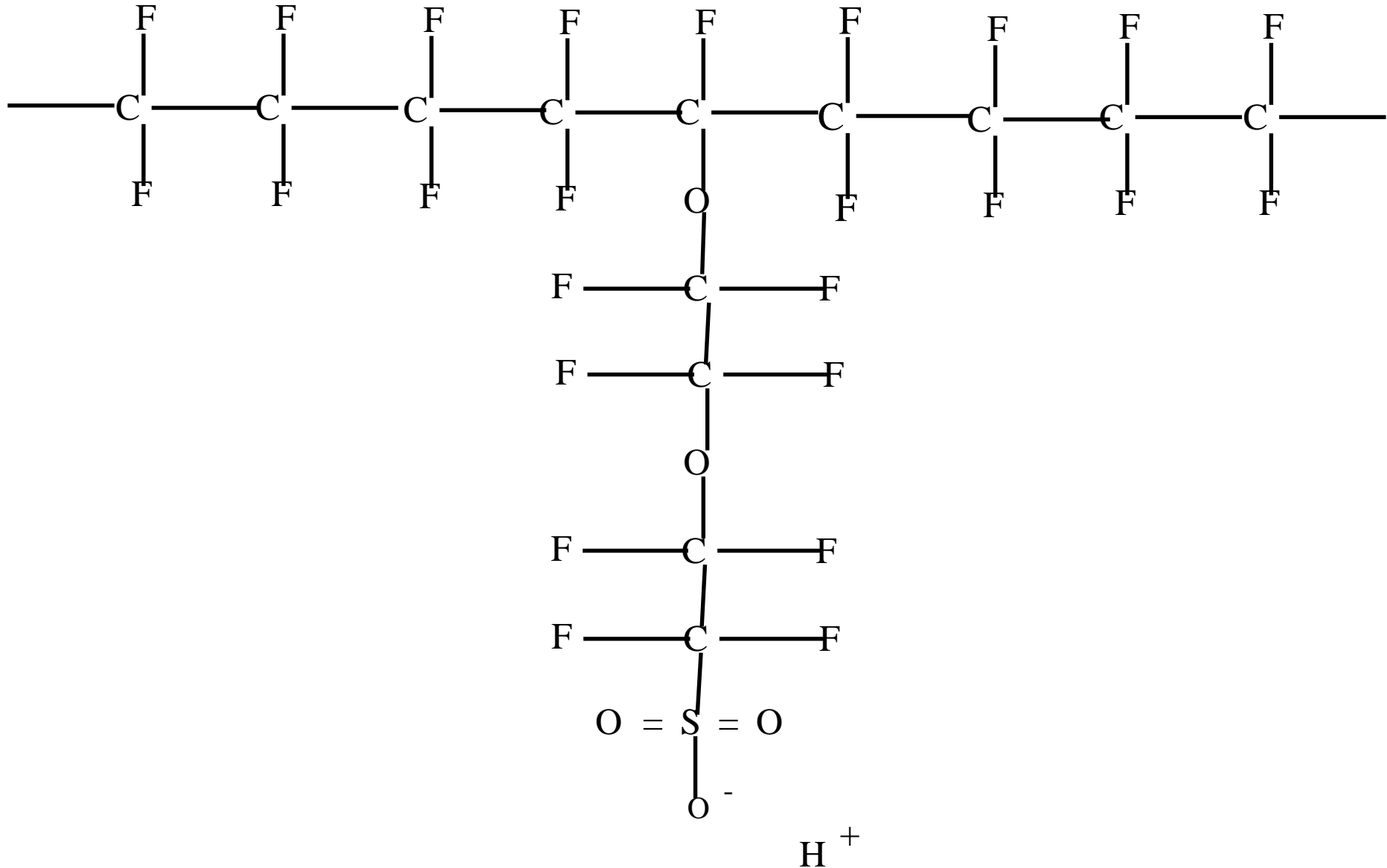- Charge-carrier:-H$^+$

Anode reaction:

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

Cathode reaction:

$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l)$

Overall reaction:-

$H_2(g) + O_2(g) \rightarrow H_2O(l)$

Differences -Similarities

Fuel cell

- Do not store chemical energy
- Reactants fed from outside the cell continuously
- Need expensive noble metal catalysts & optimum operative conditions
- Do not get discharged & no need of charging
- Never become dead as long as fresh reactants are available
- Useful for long-term electricity generation.
- Reaction products must be continuously removed
- No pollutants generated Produce power from fuels
- Significantly higher power densities

Galvanic Cell

- ✓ Store chemical energy
- ✓ Reactants from an integral part of its construction.
- ✓ These special conditions are not required
- ✓ Get-discharged when stored – up energy is exhausted.
- ✓ Limited life span in use
- ✓ Useful as portable power services.
- ✓ No such problem
- ✓ Pollutants are generated after their useful life
- ✓ They cannot generate electricity from fuels
- ✓ Lower power density

Summary

- Battery - device consisting of several galvanic cells that convert stored CE into EE.
- Batteries – primary or secondary types.
- The construction, working & applications of conventional dry cell, lead acid battery, nicad cell, lithium copper sulfide cell have been discussed .
- Fuel cell - converts the CE from a fuel into EE by oxidation process.
- Fuel cells require a constant source of fuel & oxygen /air to sustain the oxidation reaction.

Self-test

- What is the purpose of separator in a commercial cell?
- What are the disadvantages of Nicad over lead acid battery?
- What are the basic commercial requirements for a primary & secondary cell?
- Distinguish between the following;
- i) Cell & battery ii) Charging & discharging
- Write the anode active material & cathode active material in the following cells; 1) Dry cell 2) lead acid cell 3) Nicad cell
- Give reason: a) Combustion of a gaseous fuel gives thermal energy where as the oxidation of the fuel in a fuel cell gives electrical energy b) In principle, secondary battery should have unlimited life, but in practice is has limited life. c) The lead acid cell doesn't need to have separate anode & cathode compartments

Metal Finishing

Contents

- Theory of electroplating

- Polarization, decomposition potential & overvoltage

- Characteristics of a good deposit

- Factors influencing the nature of deposit

- Methods of cleaning the metal surface

- Hard chromium & decorative chromium plating

- Electro-less plating – Copper plating

Learning Objectives

- Explain the theory of electroplating & factors affecting it

- Differentiate electroplating & electroless-plating

- Describe the methods of cleaning the metal surface

- Discuss the characteristics of a good deposit

- Illustrate electroplating process – Cr & Cu

Metal Finishing

Process of deposition of an adherent metallic film of a noble metal on a base metal or polymer surface

Technological Importance

Methods of Metal finishing

ELECTROPLATING

- Process in which a thin layer of coating metal is deposited on a base metal by passing d.c. through an electrolytic soln., containing the soluble salt of the coating metal

- **Theory of electroplating;** Anode, cathode, Electrolyte, Direct current

- **Mechanism of electroplating: Three steps**

1. **Bulk diffusion:** M^{n+} **(bulk)** $\rightarrow$ M^{n+} **(substrate)**
2. **Atomic layer formation**: $M^{n+} \rightarrow ne^- \rightarrow M_{ad}$
3. **Macro-deposition**: $M_{ad} + M$ **(atoms)** $\rightarrow M_{substrate}$

Schematic of electroplating bath
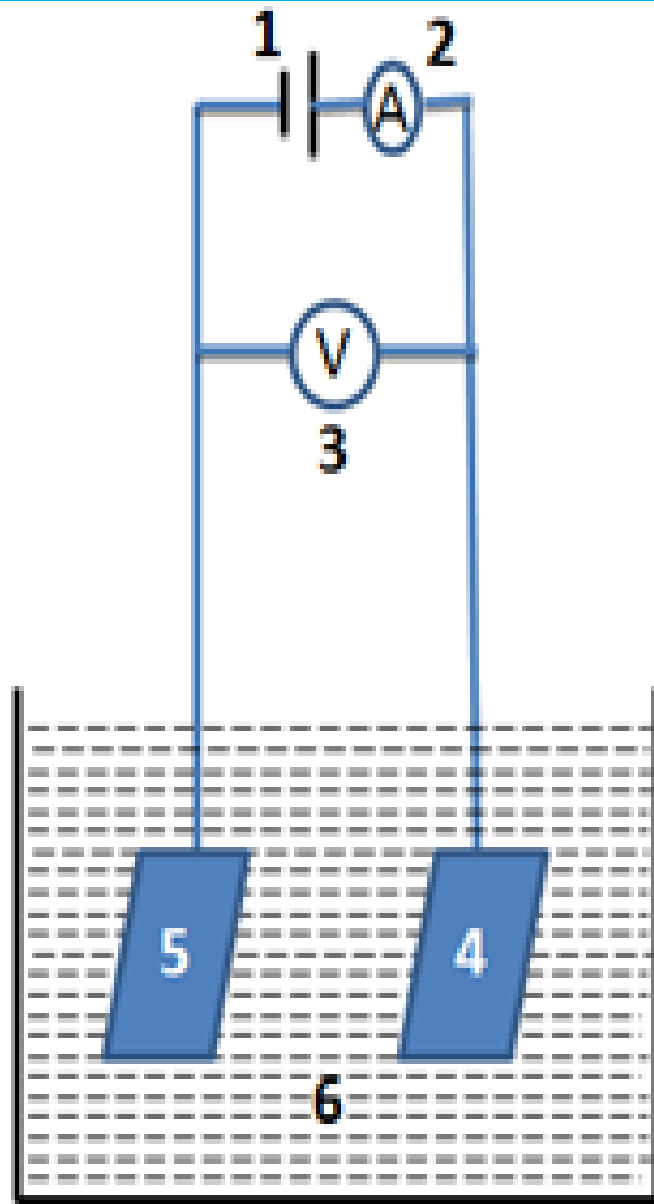
1. D.C. electrical power source
2. Ammeter
3. Voltmeter
4. Anode (Inert material or coting metal)
5. Cathode (article to be plated)
6. Electrolytic bath (solution of conducting salt, metal to be plated in a soluble form, buffer & additives)
7. Container (rubber lined steel, wood or concrete)

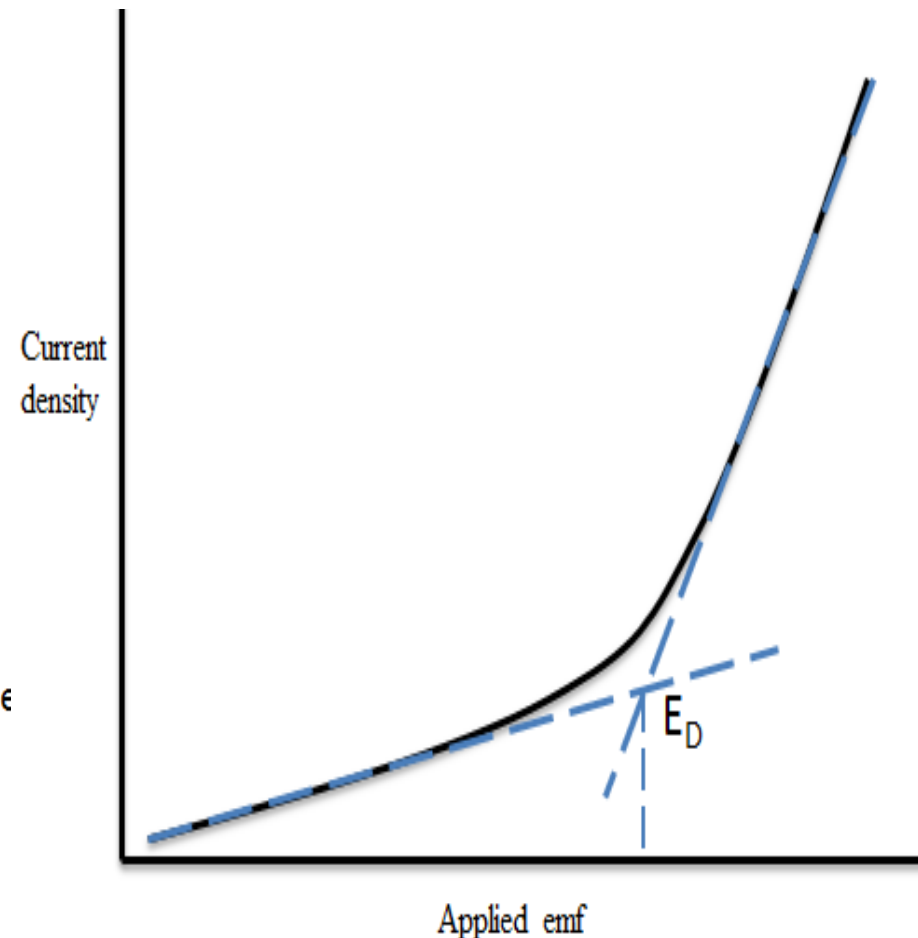# Factors Governing Electroplating

❖ Decomposition Potential (D.P.)

❖ Polarization

❖ Overvoltage

Decomposition Potential

- **Minimum external potential at which the electrolysis current begins to increase appreciably & continuous electrolysis sets in is known as decomposition potential of the electrolyte.**

- **Measurement**

B: battery
R: Rheostat
M: ammeter
V: voltmeter
E_1 and E_2: Pt. electrode

Electrolytic solution

Current density

Applied emf

E_D
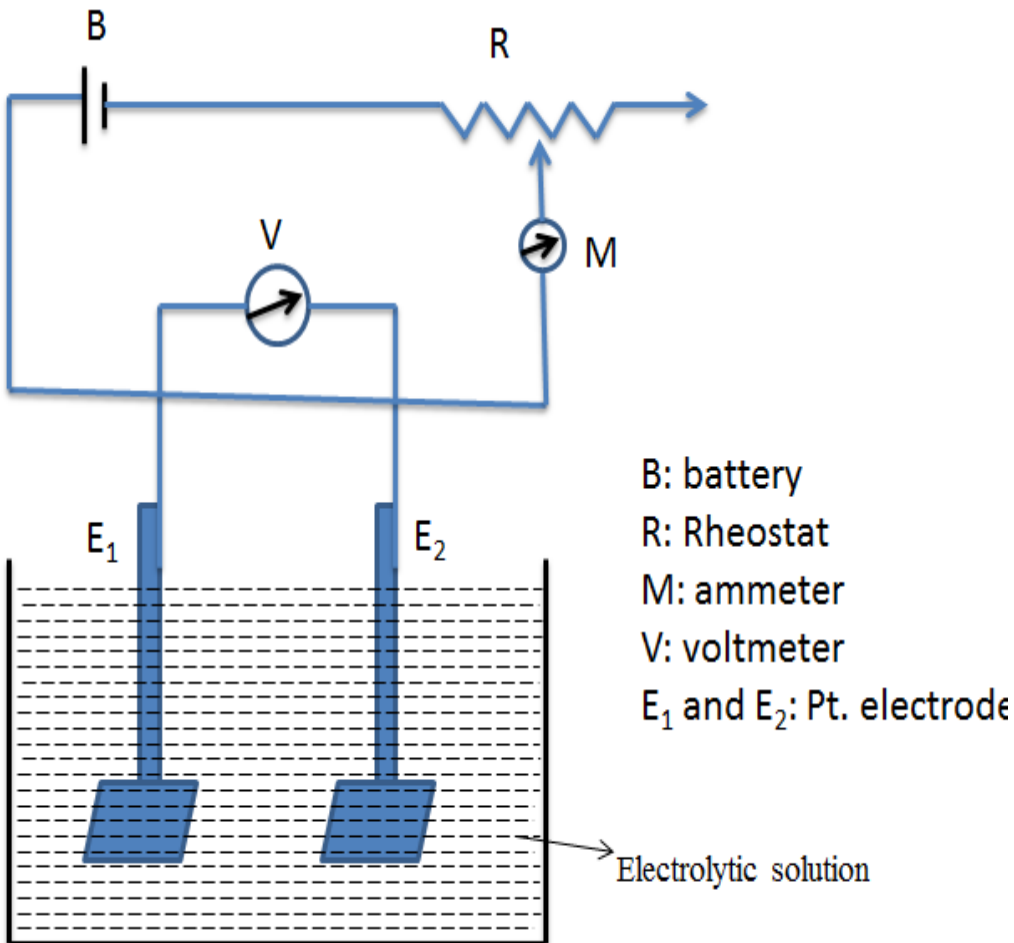
Factor affecting DP

- Strength of the current flowing through the cell

- Chemical nature of the electrodes

- Physical nature of the electrodes

- Activity of the electrolyte

- Absolute temperature

- Uses of DP → See footnote

Overvoltage

- Difference between the actual applied emf to bring about continuous electrolysis & the theoretical emf needed for such electrolysis.

- **Factors affecting overvoltage:**

- Nature & physical state of the electrodes
- Current density
- Temperature
- Nature of the electrolyte
- Nature of the material deposited

Polarization

- EMF required for the electrolysis will be greater than the reversible EMF of the corresponding galvanic cell. An electrolytic cell that requires excess voltage over the theoretical is said to be polarized & the phenomenon is called polarization.

✓ **Concentration polarization**

✓ **Kinetic polarization**

- Factors

- Importance

Characteristics of a good deposit

* should be bright & lustrous

* should be uniform, non-porous & have good adhesion

- should be hard & ductile

- should have fine grained structure

Factors affecting the nature of deposit:

✓ Current density

✓ Plating bath

✓ pH

✓ Additives:

✓ Throwing power

✓ Selection of material

Methods of cleaning the metal surface

- Physical   cleaning

- Chemical Cleaning

- Mechanical Cleaning

- Pickling

- Electro-polishing

Electroplating of chromium

	Decorative coating	Hard coating
Bath composition	Chromic acid (250 g) + H_2SO_4 (2.5 g) + Trivalent chromium(1g)	Chromic acid (250 g) + H_2SO_4(2.5g)+ Trivalent-chromium(1g)
Operating temp.	313-328 K	313-328 K
Anode	Insoluble Pb-Sn alloy	Insoluble Pb-Sn alloy
Cathode	Article to be coated	Article to be coated
Current density	20-40 mA/cm^2	30-60 mA/cm^2
Cathode efficiency	10 - 15	17 – 21
Applications	Decorative applns with corrosion resistance finish on automobiles, furniture, surgical & dental instruments	Coating of industrial components like gauges, dies, cutting tools, piston rings & hydraulic rams.

Electrolessplating

- Method of depositing a metal film on a substrate surface (conductor /non-conductor) from metal salt soln. using a suitable reducing agent without using electrical energy.

Metal ions + Reducing agent → Metal deposit + Oxidized product

- ***Process***
  - ✓ Preparation of substrate surface
  - ✓ Composition of plating bath
  - ✓ Actual reduction process
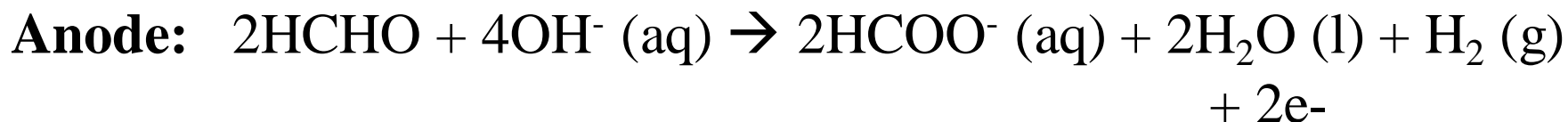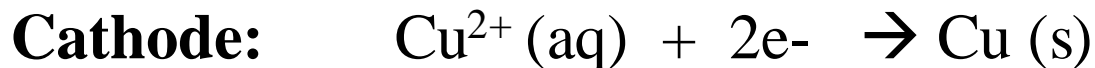
Electrolessplating

Advantages

- More uniform coating with better TP than electroplating.
- Electrical power & other accessories not required
- Coating is harder & better wear resistance
- Deposits have compatible wettability
- Superior quality deposits
- Additives, levelers or the complex filtration method not required.
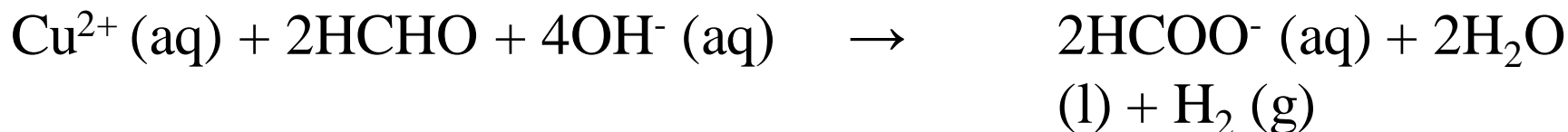- Simple equipment sufficient

Disadvantages

- Cost of waste treatment high.
- Frequency of dumping electroless bath high
- Costs per unit weight of the deposited metal are more
- Needs pure chemicals
- Chemical reductants expensive
- Metal salts & reductants are thermodynamically not stable
- Impurities, dust or colloidal particles promote decomposition of bath components

Electroless plating of copper

Cathode: Cu^{2+} (aq) + 2e- → Cu (s)

Anode: $2HCHO + 4OH^-$ (aq) → $2HCOO^-$ (aq) + $2H_2O$ (l) + H_2 (g) + 2e-

Overall reaction:

Cu^{2+} (aq) + $2HCHO + 4OH^-$ (aq) → $2HCOO^-$ (aq) + $2H_2O$ (l) + H_2 (g)

Since Cu^{2+} ions & HCHO are consumed during the redox reaction, these are replenished periodically. The redox reaction involves consumption of hydroxyl ions & pH of the solution decreases as the reaction progresses. Hence addition of buffer is essential. Usual plating rate is 1-5 μmh^{-1}.

Electroless plating of Copper

Compts. of electroless-plating bath	Bath (A)	Bath (B)
Electroactive metal salt; Copper sulfate	30	12
Sodium hydroxide (basic medium)	40	15
Rochelle salt (buffer)	140	55
Sodium carbonate	25	-
EDTA-Sodium salt(chelating-agent)	17	-
Formaldehyde (reducing agent)	170	35
Temperature	RT	RT
pH	~12.0	~12.0
Rate of deposition	20	2.5

Comparison of electroplating & electroless plating

Particulars	Electroplating	Electrolessplating
Driving force	Electrical energy	Decrease in free energy of the redox reaction
Cathodic Reaction	$M^{n+} + ne^- \rightarrow M$	$M^{n+} + ne^- \rightarrow M$
Cathode	Article to be plated	Article to be plated with catalytic surface
Anode	Separate anode	Reducing agent in the soln.
Nature of deposit	Pure metal or alloy	Metal with reducing agent & oxidized products as impurities
Thickness-limit (μm)	1 - 100	1 – 100
Applicability	Applicable to conductors only	Can be used for conductors & non-conductors
Throwing power (TP)	Less TP; cannot be used for irregular shapes & intricate parts	More TP; can be used for irregular & uneven shaped objects

Summary

- Metal finishing by surface modification is an important aspect of various engineering applications

- Commonly used metal finishing techniques include electroplating & electroless-plating

- Theory of electroplating, electroless-splating & the factors influencing electroplating are discussed

- Electroplating of chromium & electroless-plating of copper are illustrated

Review Questions

- 1. What is electroplating? Discuss the steps involved in electroplating

- 2. Describe the various purposes & applications of electroplating?

- 3. Define polarization. List the factors that affect it.

- 4. Explain the effect of the following on the nature of the deposit; i) current density ii) pH iii) metal ion concentration iv) throwing power

- 5. Mention the characteristics of a good deposit

- 6. Give reasons: i) Concentration polarization can be minimized by constant stirring of the electrolyte ii) DP of water is more than that required for its formation