

# Handwritten Notes On ELECTROCHEMISTRY (Part-3)



## ELECTROLYSIS

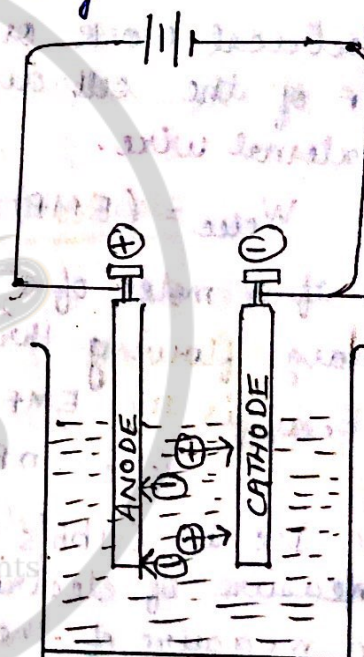
→ The process of chemical decomposition of the electrolyte by the passage of electricity through its molten or dissolved state is called electrolysis.

### → ELECTROLYTIC CELL

→ The device in which the process of electrolysis is carried out is called electrolytic cell.

→ It consists of

- i) Electrolytic tank (made of some non-conducting material like glass, wood or bakelite).
- ii) Electrolyte in its dissolved or molten state.
- iii) Source of electricity; an e.c. cell or battery.
- iv) Two metallic rods called electrodes suspended in the electrolyte & connected to the battery through conducting wires. The electrode connected to the -ve terminal of battery is a cathode while that connected to +ve terminal is a anode.



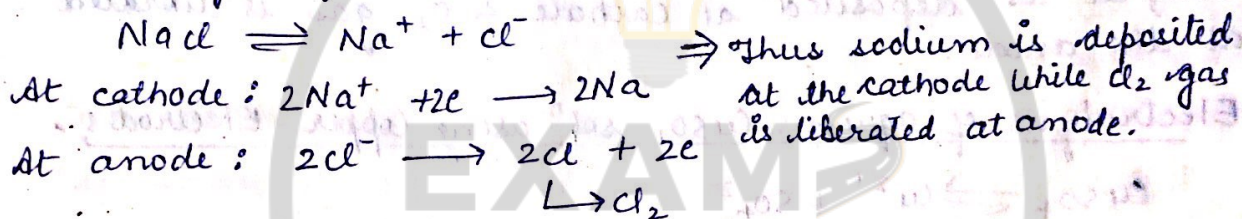
Ans. Electrolytic cell  
connected to +ve terminal



## Criteria of Product formation in Electrolysis

- The process of electrolysis can be explained on the basis of theory of ionisation. Accor. to this theory, the electrolytes are present as ions in solution and the function of electricity is only to direct these ions to their respective electrodes. The electrolytes can be electrolysed only in the dissolved or molten state.
- When electrolyte is dissolved in water, it splits up into cations and anions which on passing electric current through the solution, are attracted towards oppositely charged electrodes.
- The cations move towards -vely charged electrode while anions move towards +vely charged electrode. The formation of products at the respective electrodes is due to oxidation (loss of  $e^-$ s) at the anode & reduction (gain of  $e^-$ s) at the cathode.

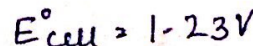
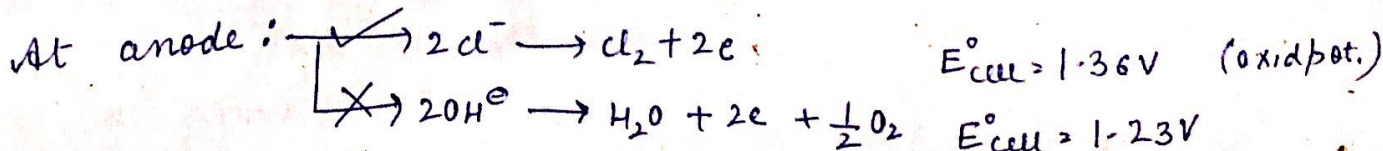
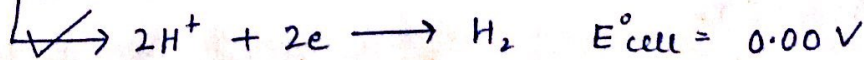
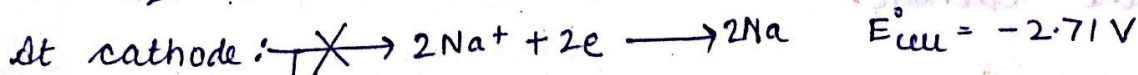
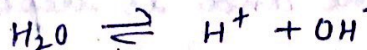
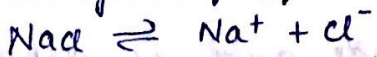
### ① Electrolysis of Molten NaCl



⇒ Thus sodium is deposited at the cathode while  $\text{Cl}_2$  gas is liberated at anode.

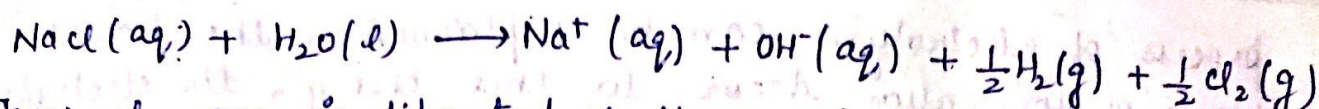
NOTE: In case there is a possibility of formation of more than one products at the electrodes, or there is a competition between the liberation of ions at the electrodes, then the products formed depends upon their respective electrode potential i.e. that species will be reduced first, which has higher reduction potential & that species will be oxidised first which have higher oxidation potential.

### ② Electrolysis of aqueous solution of NaCl



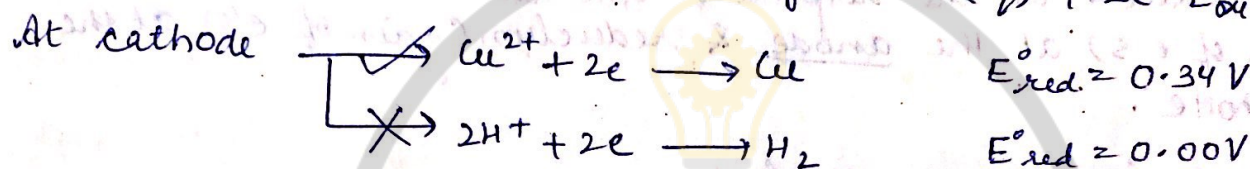
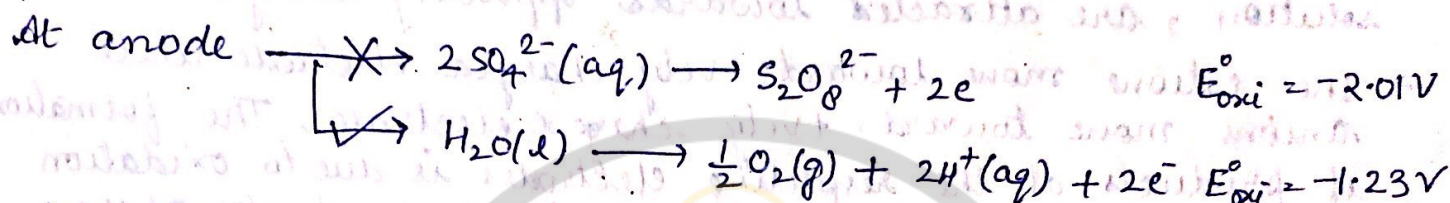
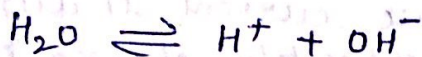
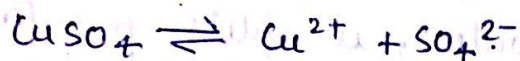


Net reaction:



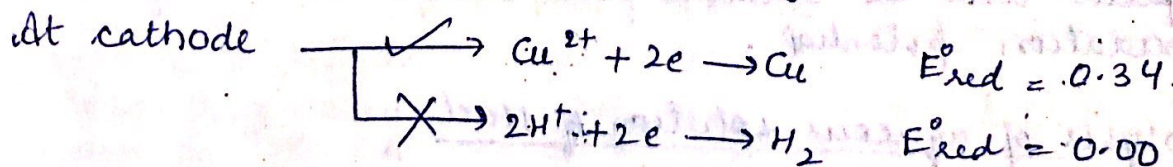
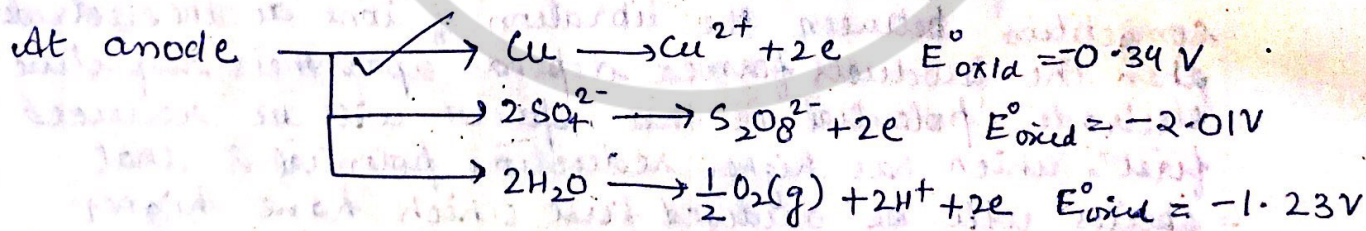
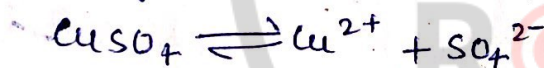
Thus,  $\text{Cl}_2$  gas is liberated at the anode whereas  $\text{H}_2$  gas is liberated at the cathode.

### ③ Electrolysis of aqueous $\text{CuSO}_4$ using Platinum Electrodes.



Thus, Cu is deposited at cathode &  $\text{O}_2$  gas is liberated at the anode.

### ④ Electrolysis of aqueous $\text{CuSO}_4$ sol<sup>n</sup> using Copper Electrodes.

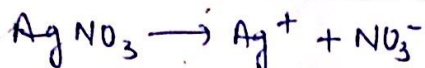


Thus copper dissolves at the anode and is deposited at the cathode.

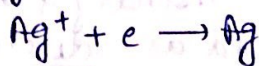




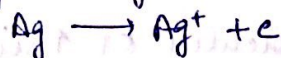
⑤ Aqueous sol<sup>n</sup> of  $\text{AgNO}_3$  with silver electrodes



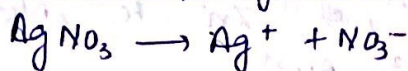
At cathode :  $\text{Ag}^+$  ion will reduce in preference to  $\text{H}_2\text{O}$



At anode :  $\text{Ag}$  will get oxidise in preference to  $\text{H}_2\text{O}$

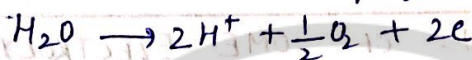


⑥ Aqueous sol<sup>n</sup> of  $\text{AgNO}_3$  with platinum electrodes

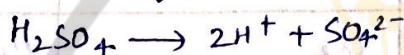


At cathode :  $\text{Ag}^+ + e^- \rightarrow \text{Ag}$

At anode :  $\text{H}_2\text{O}$  will oxidise in preference to  $\text{NO}_3^-$  ions



⑦ A dilute sol<sup>n</sup> of  $\text{H}_2\text{SO}_4$  with Platinum electrodes



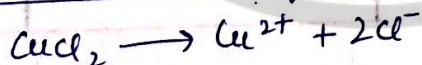
At cathode :  $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$

At anode :  $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2e$  — (1)

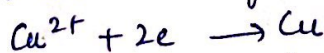
$2\text{SO}_4^{2-}(\text{aq}) \rightarrow \text{S}_2\text{O}_8^{2-}(\text{aq}) + 2e$  — (2)

For dilute sol<sup>n</sup> reaction (1) is preferred &  $\text{O}_2$  is liberated at anode but at higher conc. of  $\text{H}_2\text{SO}_4$  reaction (2) is preferred & solution of peroxodisulphuric acid ( $\text{H}_2\text{S}_2\text{O}_8$ ) is obtained

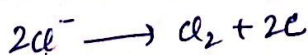
⑧ An aqueous solution of  $\text{CuCl}_2$  with platinum electrodes



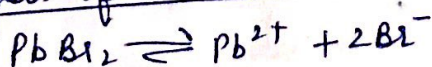
At cathode :  $\text{Cu}^{2+}$  will get reduced in preference to  $\text{H}_2\text{O}$



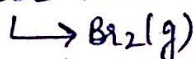
At anode :  $\text{Cl}^-$  ion will oxidise in preference to  $\text{H}_2\text{O}$



⑨ Electrolysis of molten Lead bromide using Platinum electrodes



At anode :  $2\text{Br}^- \rightarrow 2\text{Br} + 2e$



At cathode :  $\text{Pb}^{2+} + 2e \rightarrow \text{Pb}$





## QUANTITATIVE ASPECT OF ELECTROLYSIS

Consider a reaction  $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$

→ For the production of one mole of copper, 2 moles of electrons are needed.

Now charge on one  $e^-$  is  $1.602 \times 10^{-19}$  coulombs

charge on one mole of  $e^-$ s =  $1.602 \times 10^{-19} \times 6.02 \times 10^{23} = 96488 \text{ C mol}^{-1}$

This magnitude of charge =  $96488 \text{ C mol}^{-1}$  is called Faraday constant denoted by  $F$ .  
 $= 96500 \text{ C mol}^{-1}$

charge on  $n$  moles of  $e^-$ s ( $Q$ ) is given by  $Q = nF$

Thus, for  $n$  moles of  $e^-$ s, the charge equal to  $nF$  i.e.  $n \times 96500 \text{ C}$  of electricity has to be passed through the electrolyte

For a reaction,  $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$

charge equal to  $3F$  or  $3 \times 96500 \text{ C}$  has to be passed through the electrolyte.

→ Also quantity of charge flowing through the electrolyte can be calculated from the current strength & time for which the current is passed accord. to the foll. relation

$$Q = I \times t$$

$Q$  = Quantity of charge (Coulombs)

$I$  = current in amperes

$t$  = Time in seconds

## FARADAY'S LAWS OF ELECTROLYSIS

### Faraday's First law of electrolysis

Accor. to this law the mass of a substance liberated at the electrode is directly proportional to the quantity of electricity passed through the electrolyte.

$$m \propto Q$$

$$\propto I \times t$$

$$= Z \times I \times t$$

$Q$  = quantity of electricity

$I$  = current in amperes

$t$  = time in seconds

$Z$  = electrochemical equivalent (ECE)

If  $I = 1$  ampere &  $t = 1$  sec then  $m = Z$

Thus, electrochemical equivalent of a substance is the amount of substance liberated at the electrode when current of one ampere is passed through the electrolyte for one second.





## Faraday's Second law of Electrolysis

Accor. to this law,

when same quantity of electricity is passed through different electrolytes connected in series then the masses of the substances liberated at the electrodes are in the ratio of their chemical equivalent masses or the ratio of their electrochemical equivalents.

$$\rightarrow \text{chemical equivalent mass of a metal} = \frac{\text{Atomic mass}}{\text{no. of e}^- \text{ req to reduce its cation}}$$

→ Example: If two electrolytic cells A (containing  $\text{AgNO}_3$  sol<sup>n</sup>) and B (containing  $\text{CuSO}_4$  sol<sup>n</sup>) are connected in series and same quantity of electricity is passed through the cells, then the ratio of mass of copper deposited at cathode in electrolytic cell B (x g) to that of silver deposited in cell A (y g) is equal to their chemical equivalent masses.

$$\frac{M_{\text{Cu}}}{M_{\text{Ag}}} = \frac{\text{Chemical Equivalent of Cu}}{\text{Chemical Equivalent of Ag}} = \frac{Z_{\text{Cu}}}{Z_{\text{Ag}}}$$

$$\therefore \frac{x}{y} = \frac{31.75}{108}$$

$$\because \text{chemical eq mass of Cu} = \frac{63.5}{2} = 31.75$$

since  $\text{Cu}^{2+}$  req.  $2\text{e}^-$  to form Cu &  $\text{Ag}^+$  req.  $1\text{e}^-$  to form Ag

Difference in electrolytic cell and galvanic cell

Electrochemical cell	Electrolytic cell
1. Converts chemical E into electrical Energy	→ convert electrical E into chemical Energy.
2. Anode is -ve & cathode is +ve	→ Anode is +ve & cathode is -ve
3. Ions are discharged only at the cathode	→ Ions are discharged on both the electrodes.
4. Conc. of anodic half cell ↑ & cathodic half cell ↓ when the two electrodes are joined by wire	→ Conc. of electrolyte ↓ when the electric current is passed.
5. Both the electrodes are fitted in diff. compartments	→ Both the electrodes are fitted in the same compartment.
6. Redox reaction is spontaneous	→ Redox reaction is non-spontaneous
7. Electrons flow from anode to cathode in external circuit	→ Electrons supplied by the external battery & enter through cathode & come out through anode.





# TYPES OF GALVANIC CELLS

## PRIMARY

→ Become dead over a period of time & the chemical react. stops.

→ Cannot be recharged

→ Example: Dry cell  
Mercury cell

## SECONDARY

→ Can be recharged by passing D.C. & can be used again

→ Lead storage battery  
→ NiCad battery

## FUEL CELLS

→ Continuous source of Energy.

→  $H_2O_2$  fuel cell  
→ Propane-oxygen fuel cell

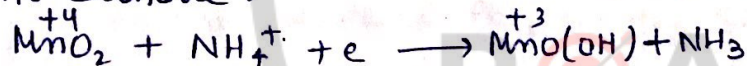
## PRIMARY CELLS

### 1. DRY CELL

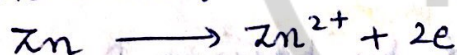
→ In this cell, anode consist of Zinc container while cathode is a graphite rod surrounded by powdered  $MnO_2$  and carbon. The space between the electrodes is filled with the paste of  $NH_4Cl$  and  $ZnCl_2$ .

→ The reactions taking place at the electrodes are as follows:-

At cathode:



At Anode:



→ The zinc ions ( $Zn^{2+}$ ) so produced combine with ammonia liberated in cathodic reaction to form diammine zinc (II) cation.

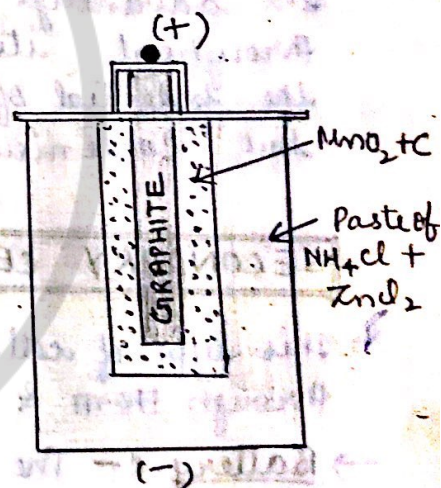
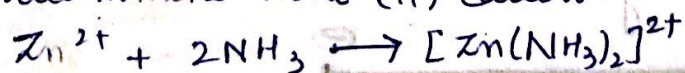


Fig: A Dry cell

→ Dry cells do not have long life as  $NH_4Cl$  which is acidic, corrodes the zinc container even if the cell is not in use.

→ The cell potential of dry cells lies in the range 1.25V to 1.5

→ There are many varieties of dry cells such as silver cell or lithium cells.

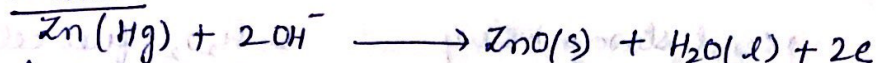
→ These are used in torches, toys, flash lights, calculators, tape recorders & many other devices.



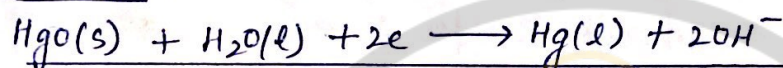
## MERCURY CELL

- It is a miniature cell which finds a frequent use these days to supply energy for watches, video cameras, hearing aids and other compact devices.
- In mercury cell the anode is zinc-mercury amalgam & the cathode is a paste of mercury(II) oxide and carbon. Electrolyte is a moist paste of  $\text{KOH-ZnO}$ .
- The operating voltage of mercury cell is  $\approx 1.35\text{V}$  and the cell reactions are as follows:

Anode:



Cathode:



Net reaction



- In this case, overall cell reaction does not involve any ion in solution whose conc. can change. ∴ it has the advantage that its potential remains almost constant throughout its life. It is a special feature. By contrast, the potential of the ordinary dry cell decreases slowly but continuously as it is used.

## SECONDARY CELLS

- This type of cells can be recharged by passing D.C. through them & can be used again and again.
- Battery :- The combination of two or more galvanic cells in series is called battery.

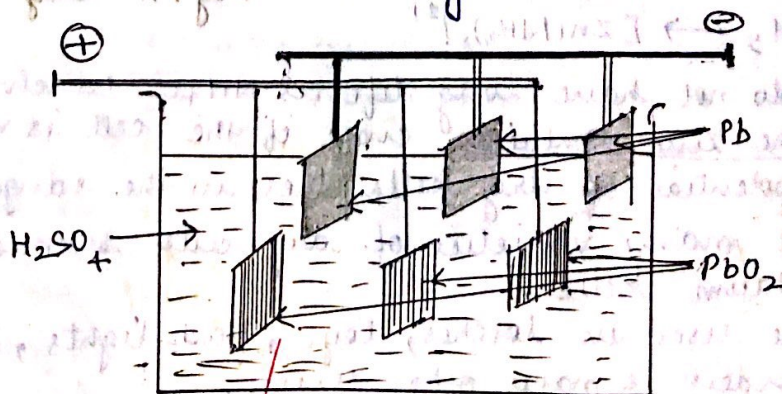


Fig: Lead storage cell



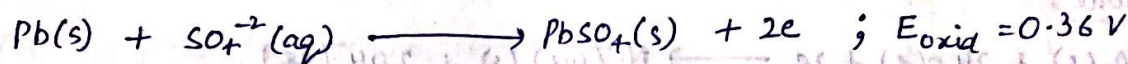


## Lead-storage battery

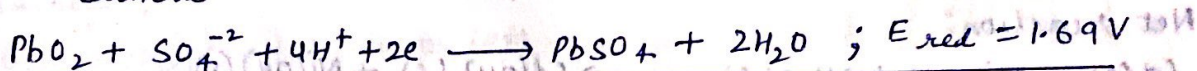
- Most frequently used battery in automobiles.
- Consist of six voltaic cells connected in series.
- In each cell anode is made of spongy lead & cathode is a grid of lead packed with lead dioxide ( $PbO_2$ ). The electrolyte is the aqueous solution of  $H_2SO_4$  which is 38% by mass.

### Reactions :-

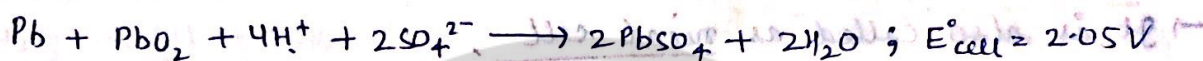
At anode :



At cathode



Net reaction :



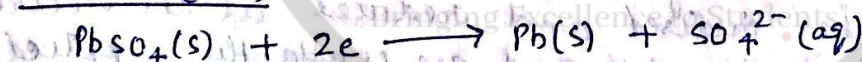
- On continuous formation of water, density of  $H_2SO_4$  decrease & when density reaches to 1.20 gm/ml, battery requires recharging.

### Recharging the battery :-

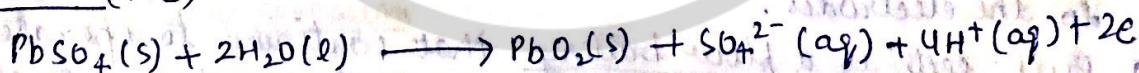
The battery can be recharged by connecting it to an external source of DC with voltage greater than 12 V. It forces the  $e^-$ s to flow in opp. directions resulting in the deposition of Pb on the anode &  $PbO_2$  on the cathode.

- During recharging, the cell behaves as electrolytic cell.

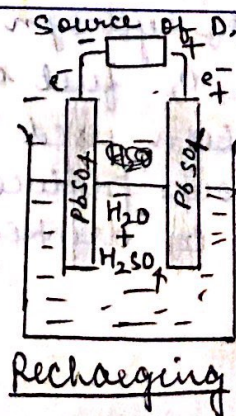
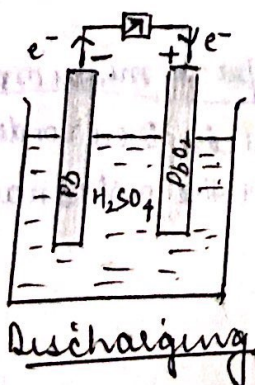
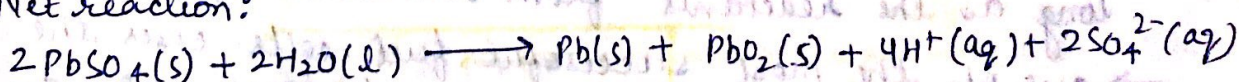
Cathode (-ve)



Anode (+ve)



Net reaction :





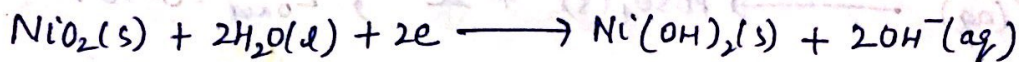
## Nickel - cadmium Storage cell

- It is a rechargeable cell.
- It consists of cadmium anode and the cathode is made of metal grid containing nickel(IV) oxide. These are immersed in  $\text{KOH}$  solution. The reactions occurring are-

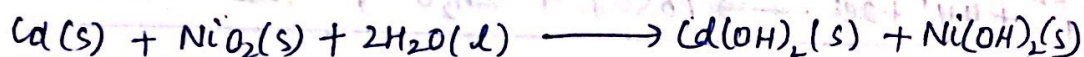
Anode:



Cathode:



Net reaction:



- It is also called as nicad cell.
- It has cell voltage  $\approx 1.4\text{V}$
- The cell is becoming more popular these days and finds use in electronic watches and calculators.

## FUEL CELLS

- In these cells, chemical energy of a fuel is directly converted into electrical energy.
- Electrical cells that are designed to convert the free E from the combustion of fuels such as hydrogen, CO or methane directly into electrical energy are called FUEL CELLS.
- These cells are designed in such a way that the materials to be oxidised and reduced at the electrodes are stored outside the cell and are constantly supplied to the electrodes.
- Fuel cell is a flow battery that continues to operate as long as the reactants from outside are fed into it.
- One of the most successful fuel cells uses the reaction of hydrogen & oxygen to form water and is k/a  $\text{H}_2\text{-O}_2$  fuel cell (Bacon cell)
- It had been used to power Apollo space missions. The  $\text{H}_2\text{O}$  vapours produced during the reaction were condensed and added to drinking water supply for the astronauts.

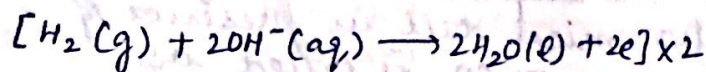




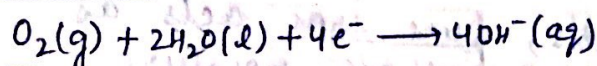
→ The cell consists of porous carbon electrodes which are impregnated with catalyst (Pt, Ag or Cu). Hydrogen & oxygen are bubbled through the electrodes into electrolyte which is an aq. solution of NaOH or KOH.

→ The electrode reactions are:

Anode:



Cathode:



Net reaction:

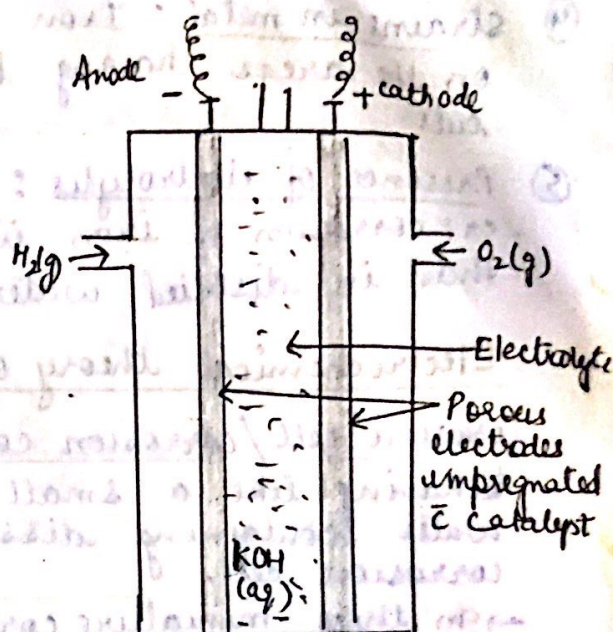
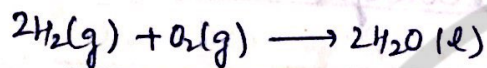


Fig: A single alkaline cell

→ The cell runs continuously as long as the gases  $H_2$  &  $O_2$  are supplied at the temp 525 K & 50 atm. pressure.

### Advantages of fuel cells

- 1) Pollution free working
- 2) High efficiency (70-75%)
- 3) Continuous source of Energy

## CORROSION

→ Corrosion may be defined as the process of slow conversion of metals into their undesirable compounds (usually oxides) by reaction with moisture and other gases present in the atmosphere.

### Factors affecting corrosion

- ① Reactivity of the metal: More active metals are more prone to corrosion.
- ② Presence of impurities: These help in setting up a corrosion cell and makes the corrosion to occur rapidly. ex. Pure iron does not rust.
- ③ Air & moisture: The presence of gases like  $CO_2$  &  $SO_2$  in air makes it still rapid. ex: no rusting of iron in vacuum.



- ④ strains in metal : Iron articles rusting is more pronounced on the areas having bends, dents, scratches, nicks and cuts.
- ⑤ Presence of electrolytes : Electrolytes ↑ the rate of corrosion.  
ex: corrosion of iron in water takes place to large extent than in distilled water.

### Electrochemical theory of rusting

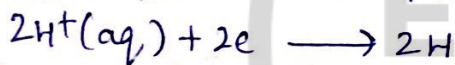
Corrosion cell/corrosion couple : The impure iron surface behaving like a small electrochemical cell in presence of water containing dissolved oxygen or  $\text{CO}_2$  is called as corrosion cell.

→ In these miniature corrosion cells, pure iron acts as anode & impure surfaces act as cathode. Moisture having dissolved  $\text{O}_2$  or  $\text{CO}_2$  constitutes electrolytic solution.

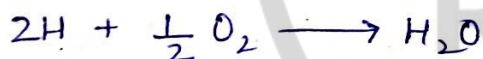
At anode :



At cathode



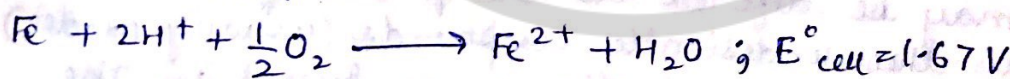
The H atoms thus produced reduce the dissolved oxygen as.



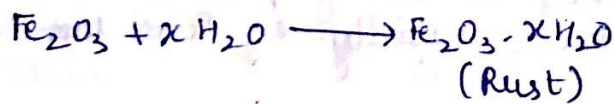
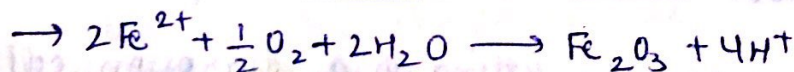
Net reduction process at cathode is



Net reaction:



→ The ferrous ions so formed moved through water & come at the surface of iron object where these are further oxidised to  $\text{Fe}^{3+}$  by atm.  $\text{O}_2$  & constitute rust which is hydrated iron (III) oxide.





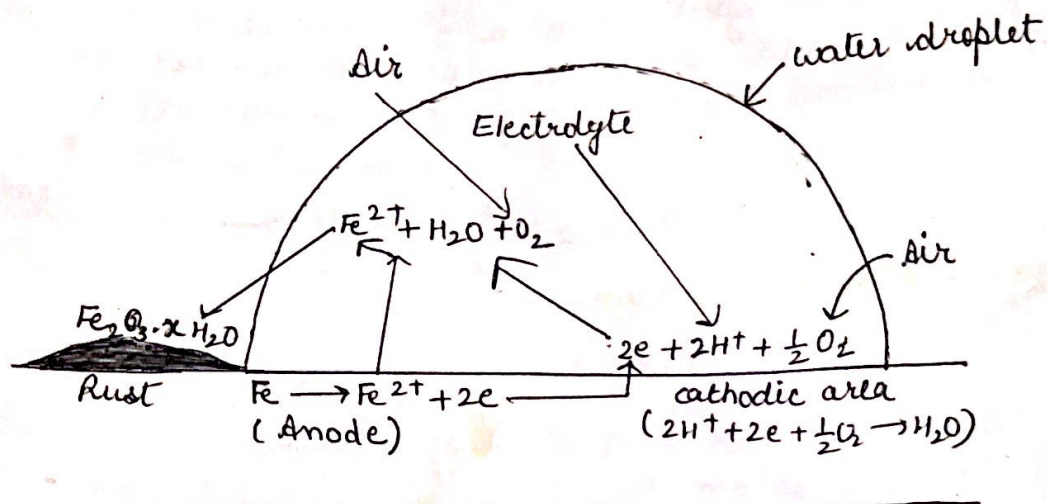


Fig: Rusting of iron

### Prevention of Corrosion

#### 1) Barrier Protection

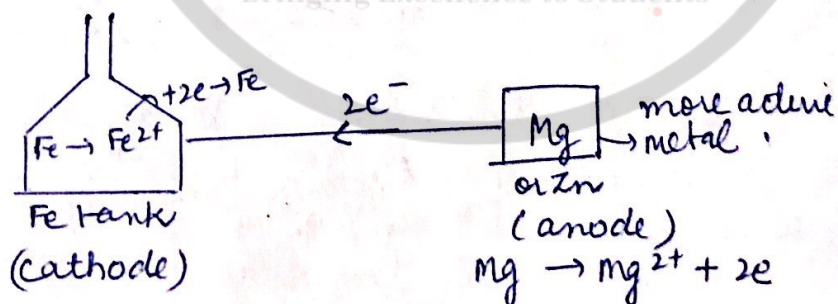
- By painting the surface
- by coating the surface with a thin film of oil or grease.
- by electroplating iron with some non-corrosive metal such as Ni, Cr, Cu etc.

#### 2. Sacrificial Protection

→ Surface of iron is coated with metal having higher oxidation potential. eg → Galvanisation: coating of Zn on iron surface.

#### 3. Electrical Protection / cathodic protection

→ In this process the Fe tank is connected with Mg metal as



#### 4. Use of anti-rust solutions

→ the alkaline solutions of some phosphate & chromate salts act as anti-rust solutions. These solutions neutralise the  $H^+$  ions which formed from the electrolyte (moisture on Fe surface) thus there is no reaction of Fe with  $H^+$  ions & rusting is prevented.