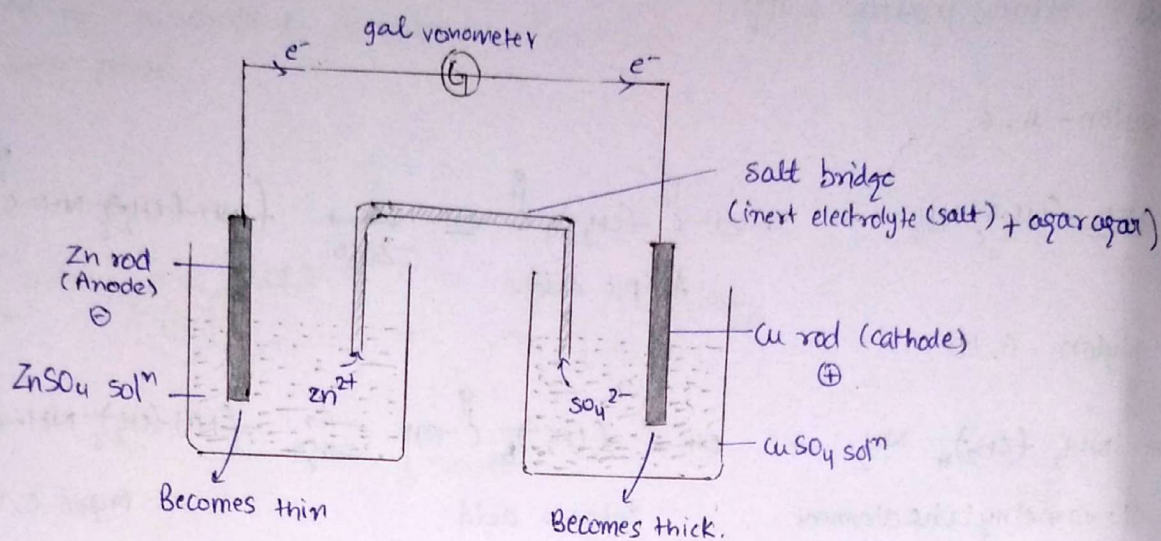


# ELECTROCHEMISTRY.

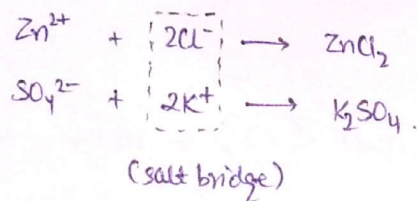
## \* Electrochemical cell.

It is a device which converts chemical energy into electrical energy & it is a combination of two half cells in which indirect redox rx<sup>n</sup> takes place.

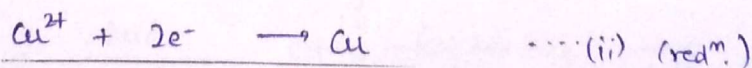
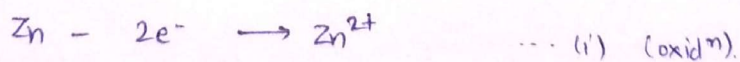


## \* Features of Electrochemical cell.

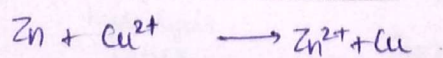
- Simultaneous redox rx<sup>n</sup> takes place.
- Direction of deflection of Galvanometer indicates flow of e<sup>-</sup> from Zn to Cu.
- Zn loses mass gradually and becomes thin whereas Cu rod gain mass & becomes thick.
- Solutions in two half-cells remains electrically neutral.



- Reactions as well as flow of e<sup>-</sup> stops after sometime.
- Reactions taking place in e-cell are:



Net cell rx<sup>n</sup>:



$$n=2$$

## \* Functions of salt bridge.

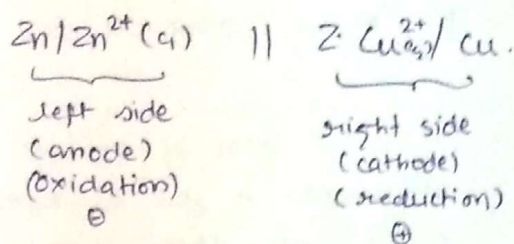
- 1) It maintains the electrical neutrality of sol<sup>n</sup> in two half cells.
- 2) It allows flow of electricity by completing the internal circuit.



NOTE: Function of Agar-Agar is to convert mixture into semi-solid.

- In salt-bridge, only inert electrolytes are used ( $KCl$ ,  $KNO_3$  etc.) because their ions cannot be oxidised or reduced.
- Carrier of current in e-cell are ions.

\* Representation of Electrochemical cell.



where  $c_1$  = conc<sup>n</sup> of  $ZnSO_4$  sol<sup>n</sup> } in mol/L.  
 $c_2$  = conc. of  $CuSO_4$  sol.

\* Electrode potential / cell potential / emf of an e-cell.

In e-cell,  $e^-$  froms electrode of higher oxidation potential (anode) flows to electrode of lower oxidation potential (cathode). The potential diff. b/w two electrodes in an e-cell is called emf.

$$E_{cell}^{\ominus} = E_{cathode}^{\ominus} - E_{anode}^{\ominus}$$

\* BATTERY: It consists of a no. of cells connected in series that can be used for producing direct current at constant voltage.

\* BATTERY CHARACTERISTICS.

- Types of Batteries.

Primary	Secondary
Not Rechargeable	Rechargeable (can be recharged by applying current in reverse direction).
Electrochemical rx <sup>n</sup> s taking place are not revers.	Electrochemical rx <sup>n</sup> are reversible.
Cell is operated untill active component gets exhausted at the electrode.	Active components are regenerated at the electrodes.
eg dry cells, mercury cells. (used in watches, calculators and toys).	eg: Lead-acid Battery (used in inverters, car batteries etc.)
ADVANTAGES: Inexpensive, convenient & light weight.	ADVANTAGES: reusability, high power density, good low temperature performance.
DISADVANTAGES: Can be used only once. Lead to waste.	DISADVANTAGES: High initial cost and maintenance charges & safety issues.



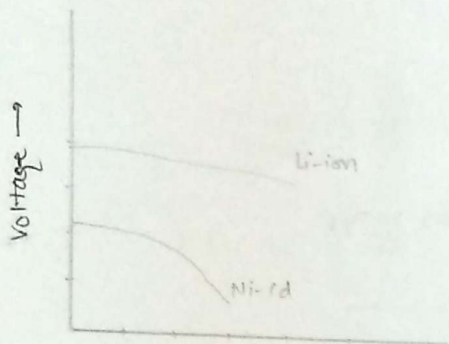
- VOLTAGE: The theoretical standard cell voltage can be calculated using electrochemical series using  $E^\ominus$  values.

$$E_{\text{cell}}^\ominus = E_{\text{cath}}^\ominus - E_{\text{anode}}^\ominus$$

But actual voltage produced will always be lower than the theoretical voltage due to internal resistance drops (IR drops).

Minimum the difference b/w theoretical & Actual value, better is the battery. Voltage value range from 1.2V for Ni/Cd Battery to 3.7V for Li-ion battery.

- DISCHARGE CURVE:



It is a plot of voltage against % capacity discharged. A flat discharge curve is desired as it means that voltage remains almost constant as it is used up.

% capacity discharged. →

- CAPACITY: Theoretically, it is the quantity of electricity involved in the electrochemical reaction. It is denoted by  $Q$ .

$$Q = x n F$$

where  $x$  = no. of moles of  $xx^n$ .

$n$  = no. of  $e^-$  transferred per mole of  $xx^n$ .

$F$  = Faraday's constant.

- Energy density: Energy derived per unit volume of the cell.

Li ion → 210 & Ni-cd = 140

Higher is the energy density, better is the battery.

- Specific energy density: Energy derived per unit weight of cell.
- Power density: power derived per unit weight of cell.
- Temperature dependence: The rate of reactions occurring depends on temp. A low Temp. gives high internal resistance and might freeze the electrolyte causing ion's movement to impede resulting in low voltage. High temp. may initiate unwanted  $xx^n$ .
- Service-life: for a secondary battery, it is defined as no. of charge/discharge cycles it can undergo before its capacity falls to 80% of its original capacity. It is b/w 500-1200.

Reasons for premature death:

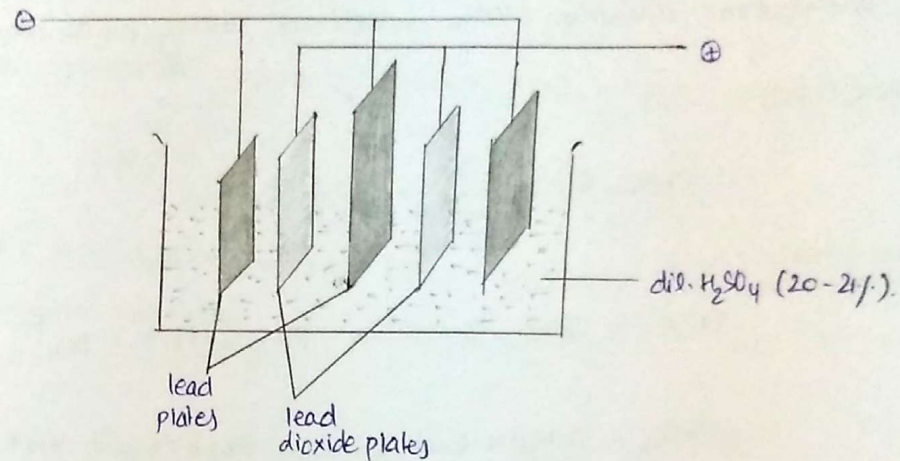
- overcharging / overdischarging
- short-circuiting
- physical shock
- extreme temp.
- Drawing more current than its capacity.



- Physical requirements: It includes geometry of battery, shape, size and weight.
- Cost: It includes initial cost, maintenance charges & cost of charging.

\* **STORAGE CELL:** A storage cell is one that can operate as voltaic cell as well as an electrolytic cell.

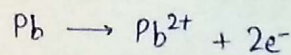
\* **LEAD-ACID STORAGE CELL:**  
(LEAD ACCUMULATOR)



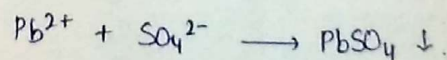
**CONSTRUCTION:** One of the electrodes is made up of lead. The other electrode is made up of lead dioxide or a paste of lead dioxide (+) placed over a grid of lead. A no. of lead plates (-) are connected in parallel & a no. of  $PbO_2$  plates (+) are also connected in parallel. These are separated from each other by insulators like rubber. A lead plate is placed in between two  $PbO_2$  plates. Then, whole apparatus is dispersed in 20-21%  $H_2SO_4$ .

**WORKING:**

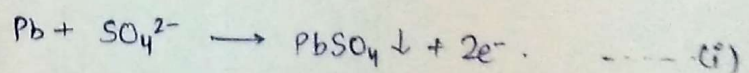
- **DISCHARGING:** When storage cell is operated as voltaic cell, it is said to be under discharging condition. Here, lead electrode loses electrons and gets oxidised at anode.



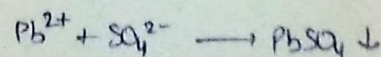
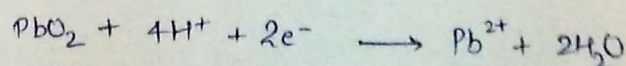
Then, released  $Pb^{2+}$  combines with  $SO_4^{2-}$ ,



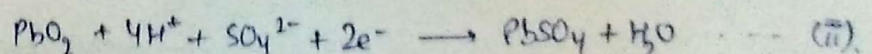
So, net anodic reaction is:



Through wire, released  $e^{-}$  from lead electrode reach  $PbO_2$  electrode & reduction occurs,

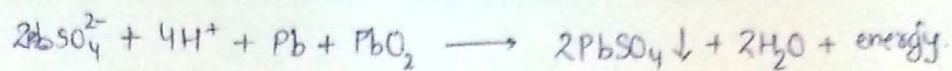


So, net cathodic rxn:



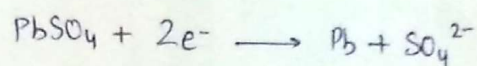


So, net discharging reaction is : (from (i) & (iii))

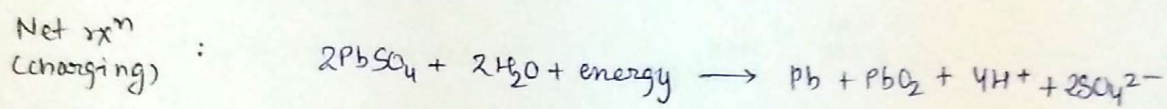


- lead sulphate is deposited at both electrodes.
- concentration of acid ↓.
- CHARGING: The storage cell no longer behaves as voltaic cell, when both electrodes get covered with  $\text{PbSO}_4$ . To recharge it, current is applied in reverse direction. The reactions taking place now are:

At cathode (-ve) :



At anode (+ve) :

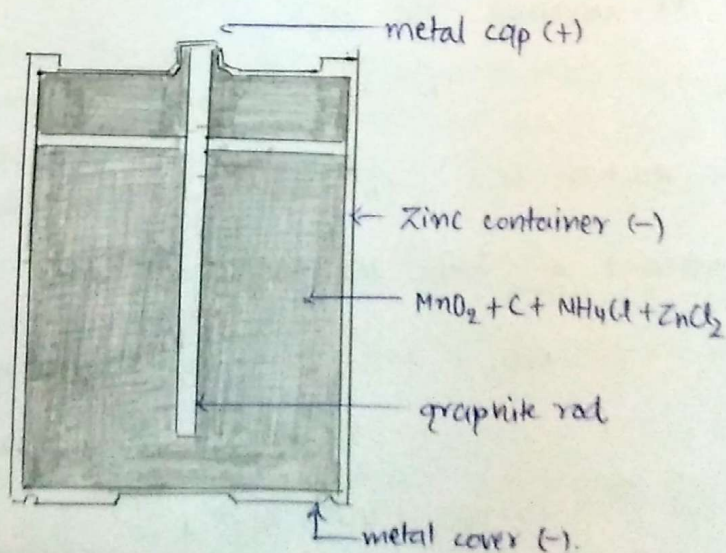


- During charging, electrodes are returned to their original condition.
- concentration of Acid increases.

USES : in electrical vehicles, gas engine ignition, railway trains, automobiles

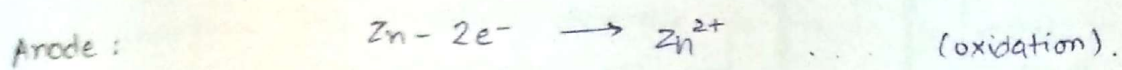
NOTE : People living in cold climate, sometimes finds trouble in starting their vehicle. The reason being that due to ↓ in temp, viscosity of fluid ↑ due to which output power is low. and vehicle may not start.

\* DRY - CELL / LECLANCHE CELL / ZINC - CARBON CELL.  
(It contains no fluid component)

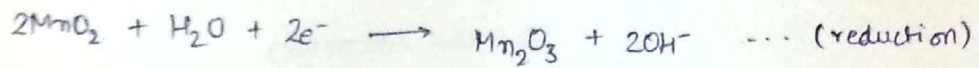




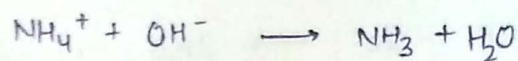
It consists of a zinc container which acts as anode a graphite rod is made as cathode, surrounded by a paste of  $\text{MnO}_2 + \text{C}$ . The electrolyte is a paste of  $\text{NH}_4\text{Cl} + \text{ZnCl}_2$  and following rxn occurs in a dry cell:



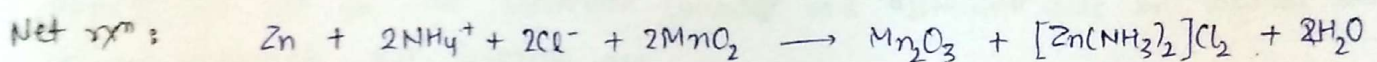
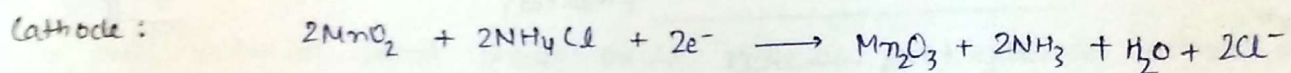
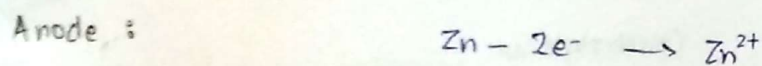
Cathode: Firstly,  $\text{MnO}_2$  is reduced to  $\text{Mn}_2\text{O}_3$  according to rxn:



Now, an acid-base reaction occurs between  $\text{NH}_4^+$  (from  $\text{NH}_4\text{Cl}$ ) &  $\text{OH}^-$ ,

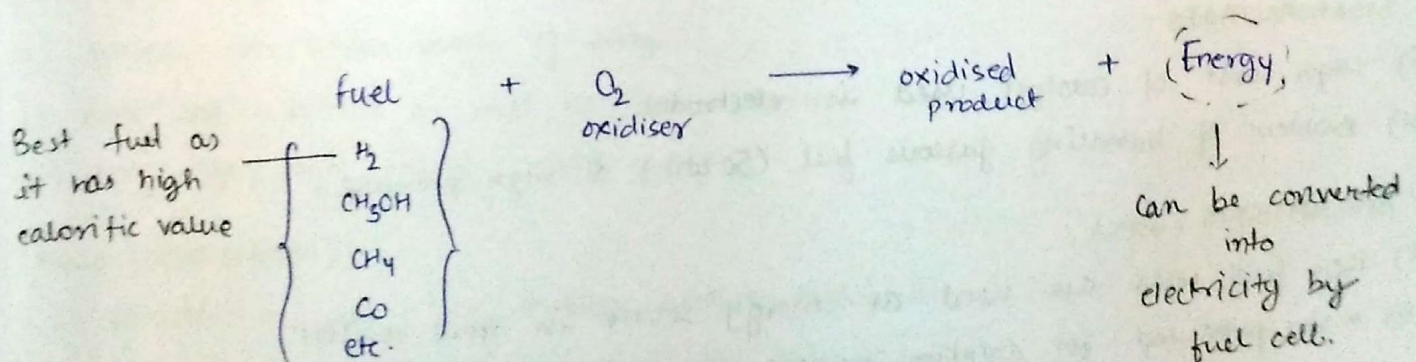


Here,  $\text{NH}_3$  produced disrupts current flow and for its prevention,  $\text{Zn}^{2+}$  (from  $\text{ZnCl}_2$ ) reacts with  $\text{NH}_3$  to form  $[\text{Zn}(\text{NH}_3)_2]\text{Cl}_2$ . So, net rxn are:

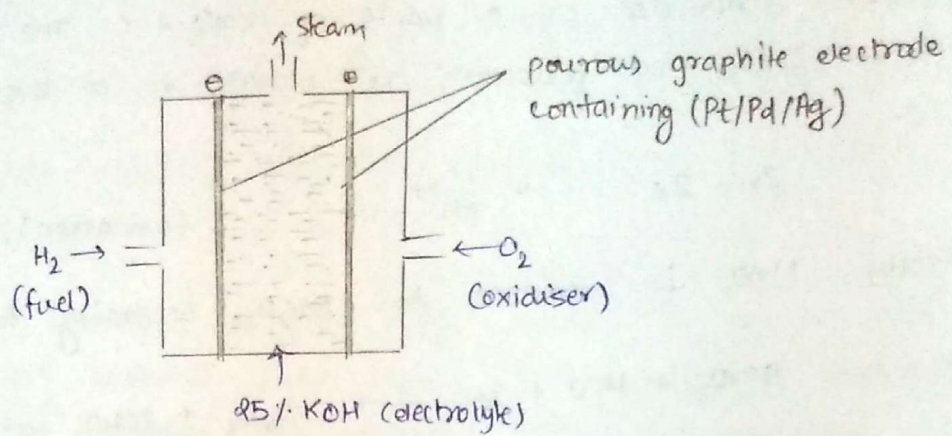


- Dry cell is a primary cell. It gives voltage about 1.5V.
- Disadvantages: i) if current is drawn rapidly from it, due to deposition of products on electrodes, output voltage decreases.  
ii) since electrolyte is acidic,  $\therefore$  zinc gets dissolved in it, and even if it is not used, cell becomes dead.
- Applications: used in flash-lights, calculators, transistor radios etc.

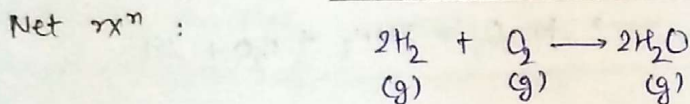
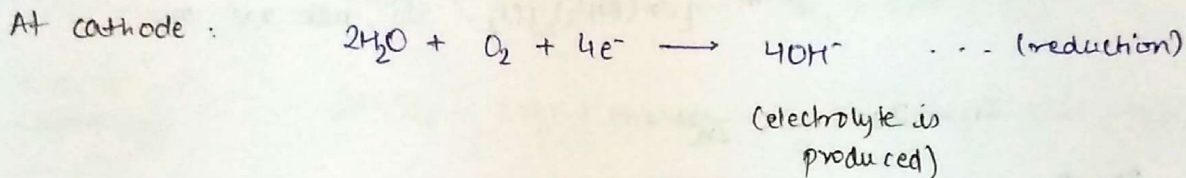
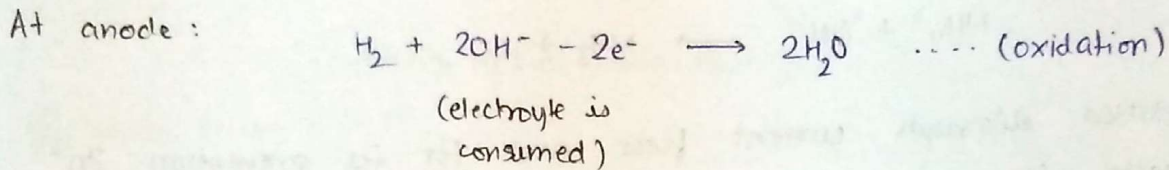
\* FUEL CELL: ( $\text{H}_2$ - $\text{O}_2$  fuel cell)







Reactions in fuel cell are :



One of the best fuel cell is  $H_2O_2$  fuel cell which converts chemical energy of fuel into electricity. In this cell,  $H_2$  and  $O_2$  are continuously passed into porous graphite electrode into KOH sol<sup>n</sup>. The catalyst like Pt/Pd/Ag are added to electrode to accelerate electrode reaction.

#### • ADVANTAGES :

- i) High efficiency (70-75%)
- ii) no pollution problem, i.e. it is ecofriendly.
- iii) the water produced can be used for drinking purpose by astronauts.
- iv) continuous source of energy.

#### • DISADVANTAGES :

- i) High cost of catalyst used in electrodes.
- ii) Problem of handling gaseous fuel (50 atm). at high pressure.

#### • APPLICATIONS (USES) :

- i)  $H_2O_2$  fuel cells are used as energy source in space vehicles.
- ii) water produced for drinking purpose.

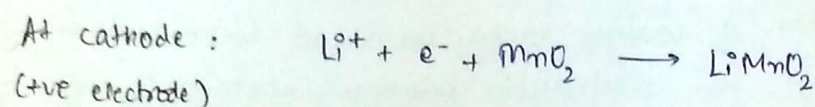
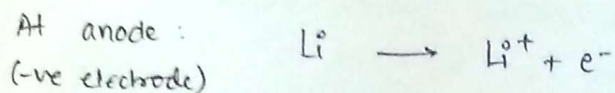


## \* LITHIUM-ION BATTERIES

Lithium ion batteries are rechargeable batteries in which lithium ions move from negative electrode to positive electrode during discharging and back when charging. The positive electrode is made of metal oxide and negative electrode is usually made up of carbon. The electrolyte is a lithium salt in organic solvent.

### i) Li-MnO<sub>2</sub> batteries

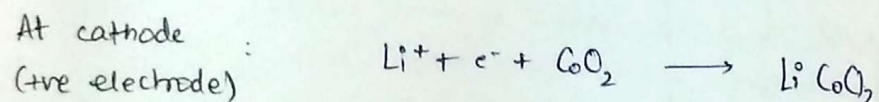
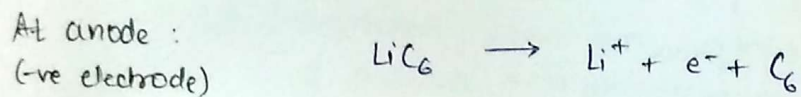
In this, lithium is anode, MnO<sub>2</sub> is cathode and lithium salt in organic solvent is an electrolyte. Rxn involved are:



} discharging rxn.  
EMF = 3 - 3.3V.

### ii) cath. Li-CoO<sub>2</sub> batteries

In this, lithium-doped cobalt oxide acts as +ve electrode (cathode) and graphite (C) acts as -ve electrode (anode) and lithium salt in organic solvent is an electrolyte. Rxn involved are:



} discharging rxn.

#### • Advantages :

- i) high energy density
- ii) Slow loss of charge when not in use. (low self discharge)
- iii) light-weight.
- iv) operate over wide range of temp.
- v) low cost. (initial as well as maintenance).
- vi) long life, light weight, quick-charging

#### • Uses (applications):

- i) In portable devices : eg: mobiles, tablets, laptops etc.
- ii) In power tools : cordless drill, hedge trimmers.
- iii) in electric vehicles : (due to light weight)



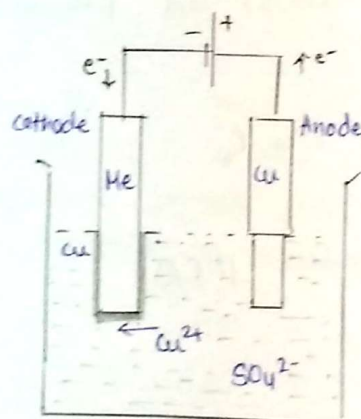
## \* DISADVANTAGES OF LITHIUM ION BATTERIES :

- i) Expensive : They are expensive to manufacture. The total product cost is around 40% higher than nickel-metal-hydrate battery.
- ii) Sensitivity to high temperature : Heat causes cells to degrade at much faster rate.
- iii) Deep discharge : deep-discharge or when voltage of battery falls below a certain level, it becomes unusable.
- iv) Safety concerns : Overheating or overcharging may cause it to explode. gases formed by electrolytic decomposition  $\uparrow$  internal pressure of cell which causes explosion.

## \* ELECTROPLATING (ELECTRODEPOSITION)

It is the process of deposition of coating metal on base metal, by passing a direct current through an electrolytic solution, containing soluble salt of coating metal.

usually, the metal to be plated is taken as cathode and anode is made of either inert metal or coating metal.



Coating of metal (Me) with copper (Cu).

In above electrolytic cell, copper is made as anode and metal to be plated is made as cathode. At anode, copper is oxidised to  $Cu^{2+}$  by losing two electrons and  $Cu^{2+}$  associates with  $SO_4^{2-}$  in the solution. At cathode, this  $Cu^{2+}$  by accepting two electrons is reduced to metallic copper. The result is effective transfer of copper from anode to cathode.

## \* OBJECTIVES OF electroplating

- for metals : i) to increase corrosion, wear resistance and resistance to chemical attacks. ii) to improve physical appearance, & surface properties. iii) to make it decorative.
- for non-metals : i) to increase surface conductivity by using non-metallic materials ii) to make it decorative iii) to  $\uparrow$  strength.



## \* CHARACTERISTICS OF ELECTRODEPOSIT.

- i) Thickness: thin coating for decorative purpose and thick coating for corrosion resistance.
- ii) Adherence: weak adherence of electrodeposit results in peeling off coating.
- iii) Hardness: measured in terms of Brinells. Hardness is 5 Brinells for lead coating and 1000 Brinells for chromium coatings.
- iv) Brightness: depends on i) smoothness of surface ii) natural reflectance of metal.
- v) Protective value: depends on porosity and thickness of coating. porosity  $\downarrow$  protective value and thickness  $\uparrow$  protective power.
- vi) Throwing power: ability of electrolytic cell to give a deposit of uniform thickness over entire cathode area. Maximum throwing power is obtained when cathode is regular in shape. Factors related to throwing power is:
  - i) conductance of bath solution: High conductance causes uniform rate of deposition
  - ii) Anodes: Uniform deposition can be attained by optimum distance placement of anodes.
  - iii) additives: complexing agent and levellers  $\uparrow$  throwing power.
- vii) Temperature: usually, bath solutions are used at temp. close to room temp., Sometimes, warm bath solutions are also used because i) solubility of electrolyte  $\uparrow \Rightarrow$  concentration of metal ion  $\uparrow \Rightarrow$  current density  $\uparrow$   
ii) due to  $\downarrow$  in crystal size, it lowers cost of electrical energy. At still higher temperatures, hydrogen gas is evolved which corrodes the equipment and decomposes organic additives.
- viii) Agitation: It should not be done to great extent, as it may lead to rough deposition,  $\downarrow$  throwing power,  $\uparrow$  in temp. of bath.
- ix) cleaning of article to be plated: Cleaning is essential before electroplating to remove dirt / grease particles which may cause weak adherence of coating.

## x) COMPOSITION OF ELECTROPLATING BATH:

- i) plating metal ion salt-solution: metal-ion conc<sup>n</sup> should be moderate (1-3 mEq/L) for thick coating, higher metal-ion conc<sup>n</sup> is required. At still higher metal-ion conc<sup>n</sup>, mass transfer process decreases which results in degradation of quality of deposit. To increase conductivity, non-participating electrolytes & inert electrodes are used.
- ii) complexing Agents: These are employed when:
  - metal-ion & cathode don't known to react, for eg. in coating on Cu on Fe



$\text{Cu}^{2+}$  is complexed with  $\text{CN}^-$  to avoid reaction,



ii) to increase throwing power.

Smooth and adherent coatings are produced, when coating of Ag, Au, Cu is done in presence of  $\text{CN}^-$ .

c) Organic Additives:

- Brighteners: These produce 'microscopic fine deposits'. The grain-size of deposits is smaller than wavelength of light,  $\therefore$  light gets reflected from its surface. eg. Aromatic sulphonates, and compounds containing  $-\text{C}\equiv\text{N}$ ,  $\text{C}=\text{O}$ ,  $-\text{N}=\text{C}=\text{S}$  (coumarin) etc.
- Levellers: Its function is to level the deposit by getting itself adsorbed on certain regions where rapid diffusion of ions occurs eg. Sodium allyl sulphate.
- Surface modifiers: They alter structure of electrodeposits & hence its properties. eg. Saccharin.
- Wetting Agents: They remove gas bubbles ( $\text{H}_2$ ) from cathode. The  $\text{H}_2$  gas gets entrapped in metal plating and make it brittle. eg. Sodium lauryl sulphate.

xi) Current density (current per unit surface area of cathode) ( $\text{Am}^{-2}$ ) ( $\text{mAcm}^{-2}$ ).  
Current density  $\uparrow$  on  $\uparrow$  applied voltage upto a limit.

- Low current density: surface diffusion process is faster than electron transfer. It results in uniform deposit.
- On  $\uparrow$  current density, surface diffusion process retards & electron transfer  $\uparrow$ . It results in less ordered deposit.
- At very high current density below limit: results in poorly adherent, rough, powdery texture deposits.

xii) choice of electrolyte: electrolyte should be good conductor, highly stable, should not undergo oxid<sup>n</sup>, red<sup>n</sup>, hydrolysis etc and should have high covering power.

xiii) pH of bath liquid:  $4 \rightarrow 6$  (pH range).

i) pH lower than optimum value causes hydrogen evolution.

ii) pH is higher than optimum value causes hydroxide formation.