$(NV)_{Fe^{+2}} = (NV)_{KMnO_4}$

$$\boxed{N_{Fe^{+2}} = \frac{(NV)_{KMnO_4}}{V_{Fe^{+2}}}}$$

$$\boxed{Wt_{Fe^{+2}} = N_{Fe^{+2}} \times 56 \ g/L}$$

20/06/2022

UNIT-2 BATTERY TECHNOLOGY

Battery

- Advantages
  Advances
- Different types
  (Applications)

* Lithium ion: laptops, mobiles, electrical vehicles.
* Lead acid battery: inverter, automobiles.
* Minimum voltage required to start an automobile : 12V
  laptop : 12-14 V

* Uni-directional batteries : Non-Rechargeable Battery
  (Galvanic cell)

* Bi-directional : Rechargeable Battery
  (Combination of cells based on the requirement)

Series: Voltage is doubled.

Parallel: current is doubled.

* **Battery:** Combination of cells (more than 1) connected either in series (or) parallel

It is a device which contains more than 1 cell which is either connected in series or parallel which undergoes redox reaction which produces electrical energy.

Eg: Zinc carbon battery; lithium ion diced, Lithium Vanadium pentaoxide (LiV_2O_5); Lead acid battery; Ni-Cd batteries

* We do not use lead acid batteries in railways instead we use Ni-Cd battery.

TYPES: In primary batteries; irreversible cells are used.

- → Primary Batteries/Non-Rechargeable
- → Secondary Batteries/Rechargeable.
- → Flow Batteries/Fuel cells.

* **Primary Batteries:**

In these cells; chemical reactions are irreversible. It acts as only GALVANIC CELL

Eg: T.V remote batteries - Zinc Carbon Battery
Wrist watches. Zinc-Ag/Mercuric Oxide

* **Secondary Batteries:**

In these cells; chemical reactions are reversible. These act as electrolytic & Galvanic ~~battery~~ cells.

eg: Lithium ion battery; Nickel-cadmium battery; lead acid battery.

* **Flow Batteries:** (Fuel cells)

It's a kind of primary battery where fuel and oxidising agents are supplied continuously at anode & cathode; due to which spontaneous redox reaction takes place & electrical energy is produced. fuel + O_2 ⟶ Product + Electrical energy

Ex: H_2-O_2 fuel cell; $C_2H_5OH-O_2$ fuel cell (extracted from food grains)

Fuel at anode (RA): H_2, C_2H_5OH, CH_3OH, LPG, CNG, CH_4

Fuel at cathode (OA): O_2, air

CH_3OH: wood alcohol (extracted from plant remains)

* **Types of cells:**

→ Reversible ⟶ Irreversible

* Cell ⟶ $\boxed{P \| S}$

$xV > yV \Rightarrow$ Galvanic Cell
$xV < yV \Rightarrow$ Electrolytic Cell
$xV = yV \Rightarrow$ No reaction

If all the 3 conditions are satisfied by a cell; it is called a reversible cell.

* If the 3 conditions are not satisfied; cell is called irreversible cell.

→ Secondary batteries are rechargeable ∴ reversible cells are used.

* Battery Characteristic Properties:

1) Free Energy Change
2) EMF
3) Power density
4) Energy density

⇒ Free energy change:

$\boxed{\Delta G^\circ = -nFE^\circ}$ ⇒ Remains same for both a cell & a battery

⇒ EMF:

$$\boxed{E_b = E_b^\circ - \frac{0.059}{n} \log \frac{[P]}{[R]}}$$

⇒ Power density: Power produced per unit mass

$\boxed{P = VI}$ watt

$\boxed{\frac{P}{mass} = \frac{VI}{m}}$ W/kg

⇒ Energy density: Energy per unit mass (or) volume

$E = P \times t$

$\frac{E}{Mass} = \frac{P \times t}{mass}$ J/kg

$\frac{E}{Volume} = \frac{P \times t}{Volume}$ J/m³

* Free energy change of a battery:

→ For a primary battery; $\Delta G = -ve$

→ For a secondary battery $\Delta G = -ve$ (during discharge)
$\Delta G = +ve$ (during charging)

* EMF: depends on standard EMF and concentration of electrolytic solution.

* Power density: Power produced per unit mass of battery

$\boxed{W = VA}$ W/kg

* Energy density: energy produced per unit mass (or) volume of battery.

$\boxed{Whr/kg \text{ (or) } Whr/l}$

*ENERGY & POWER RELATION: $P = \frac{E}{t}$

→ Battery (20gm) having 1.5A produces voltage of 2V for about 30minutes. Calculate Energy density & power density.

$$\text{Power density} = \frac{VI}{m} = \frac{2 \times 1.5}{\cancel{20}} \times \cancel{1000} = 150\,W/kg$$

$$\text{Energy density} = \frac{\cancel{150} \times \cancel{30}}{\cancel{60}}$$

$= 75\,J/kg$

$$= \frac{2 \times 1.5 \times 0.5}{\cancel{20}} \times \cancel{1000}$$

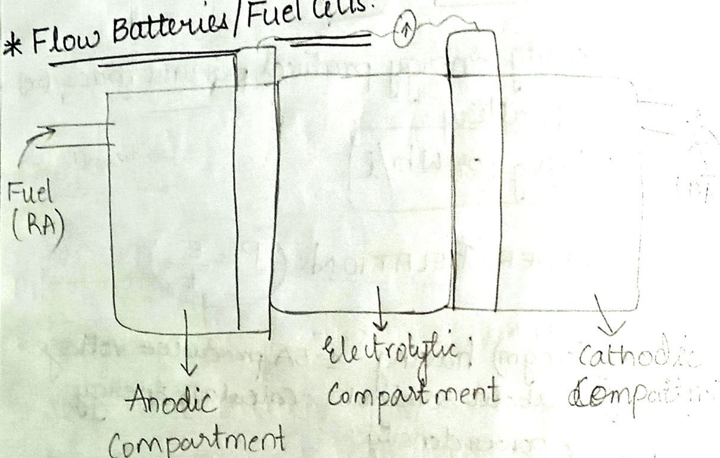
$= 75\,J/kg$

ASSIGNMENT-2
* Select any 5 batteries: minimum 2 primary and list out their voltage; ~~charge~~ : current; energy density and power density (2M). [Application

22/06/2022

PRIMARY BATTERIES:

* Flow Batteries/Fuel Cells:



* PRIMARY BATTERIES:

(Type of electrolyte used)

Alkaline Batteries (KOH)
- $K^+ + OH^-$
- Life of battery is more. (Shelf life)
- Oxidation reaction at anode is slowed down.

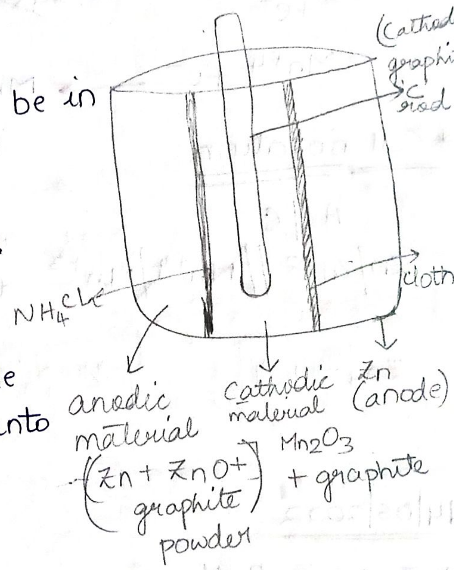
Acidic Batteries (NH_4Cl)
- $NH_4^+ + Cl^-$
- Shelf life is less compared to alkaline

Zn-C
Zn-Ag_2O
$\boxed{Li\text{-}V_2O_5}$ ⇒ Reserve Battery

* Zinc Carbon Battery / Zinc Manganese oxide battery dry cell:

- Anode & cathode of battery should never be in contact; this leads to short circuit

Redox reaction ⇒ Electrical Energy.



The anode and cathode materials are made into paste so as to avoid

reactions at anode

$$\boxed{Zn^0 \longrightarrow Zn^{+2} + 2e^-}$$

$$NH_4Cl + H_2O \longrightarrow NH_4^+ + Cl^-$$

$$\boxed{NH_4^+ \longrightarrow NH_3}$$

$$Zn^{+2} + Cl^- + NH_3 \longrightarrow (Zn(NH_3)_4)Cl_2$$

Stable Complex.

* Why Zn-C battery is not work as reversible battery? Explain

⇒ Zn forms a complex with ammonia produc from electrolyte to form a stable complex which is not reversible (Reaction).

at cathode

$Mn^{+4} + e^- \longrightarrow Mn^{+3}$ ~~×××~~

$Mn^{+4} + e^- \longrightarrow Mn^{+3}$ (Reduction)

$\boxed{Voltage = 1.5V}$

* Cell notation:

A||C

~~$Zn/Zn^{+2}//Mn^{+4}/Mn^{+3}$~~

* less cost
* High energy density.

Zn, NH_4Cl

24/06/2022

* $ZnAg_2O$ Battery: alkaline primary battery
- Also called Button-type battery.
- Ag_2O is pressed into thin button-type metal case which act as cathode.
- Absorbent material is soaked in KOH placed in b/w anodic & cathodic compartment.
- Zn metal is at the centre which acts as anode.
- KOH is electrolyte.

Anode: $Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$

Cathode: $Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^-$

$Zn + Ag_2O \longrightarrow ZnO + 2Ag + E.E$

- Battery life is almost 1 year.
- Since small in size; produces a high voltage i.e. 1.5V; and less amount of current.
- There is no voltage drop.
- Used in electronic watches, calculators & small electronic gadgets etc.
- More reliable, non-toxic.

* Lithium-Vanadium Pentoxide (Li/V_2O_5) battery:
- Primary and reserve type battery.
- Anode: lithium
- Cathode: 90% V_2O_5 & 10% graphite (weight)
- Electrolyte: 2M $LiAsF_6$ + 0.4M $LiBF_4$ in methylformate.
- Separator: micro porous polypropylene.
- Cell voltage is 3.2V
- High volumetric energy density
- controlling the reactions by removing the active part
* methyl formate: $H-\overset{\|}{C}-O-CH_3$

Anode: $Li \longrightarrow Li^+ + e^-$

Cathode: $V_2O_5 + Li^+ + e^- \longrightarrow LiV^{+5}_{2-x}V^{+4}_{x}O_5$

$V_2O_5 + Li \longrightarrow LiV^{+5}_{2-x}V^{+4}_{x}O_5 + EE$

To avoid chemical decomposition in the battery; we remove the active part i.e. electrolyte

*Limitations of Primary Battery: 27/06/2022

- Non-reversible ~~cell~~ reactions.
- High drain out applications are not possible.
- Limited shelf life.

These can be overcame by using Secondary batteries.

*SECONDARY BATTERIES:

- These are Operated in cycles i.e. recharge & discharge.
- During discharge; these act as Galvanic Cell. $[\Delta G = -ve]$ $[E_{cell} (+ve)]$ and during recharge, these act as electrolytic cell $[(\Delta G = +ve)(E_{cell} = -ve)]$

1) Acidic = Lead Acid Battery
2) Alkaline = Nickel-cadmium Battery $\Rightarrow$ N_i-metal Hydride (modified version)
3) Non-aqueous = Lithium ion Battery.

*LEAD ACID BATTERY:

Valve Regulated Lead acid Battery
Punched Battery etc.
{ Same material, Same principle but different arrangement of polymers

- Bigger in size but economically viable.

Ex. Used in invertors.

*Pb acid battery: Single = 2V
6 pairs = 12V

* Anode: Spongy Pb° (alloy of Pb & Sn)

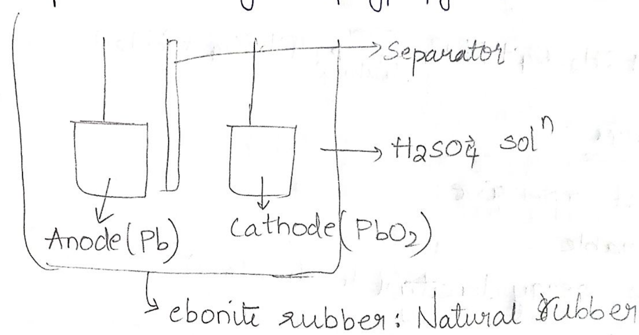
Anodic Material:

Cathode: $\overset{+4}{Pb}O_2$ (metal rod)

Cathodic Material:

Electrolyte: 25-30% of H_2SO_4 (specific gravity = 1.2)

Separator: Polymer (polypropylene) sheet.



→ During discharge: Galvanic cell.
- spontaneous redox reaction.

$$(H_2SO_4 \longrightarrow 2H^+ + SO_4^{-2}) \times 2$$

Anode: $Pb^{\circ} \longrightarrow Pb^{+2} + 2e^-$

$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4 \downarrow$ deposited on lead plate.

Cathode: $PbO_2 + 2e^- + 4H^+ \longrightarrow Pb^{+2} + 2H_2O$

$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4 \downarrow$

Cell Reaction:

$$Pb + \underbrace{2SO_4^{-2} + 4H^+}_{2H_2SO_4} + PbO_2 \longrightarrow 2PbSO_4 + 2H_2O$$

The water formed i.e. in excess will be drained out from the battery.

* In cold regions, when temp falls down -4°C the electrolytic working will reduce.

$$Pb + 2H_2SO_4 + PbO_2 \xrightarrow[\text{discharge}]{\cancel{\text{charge}}} 2PbSO_4 + 2H_2O$$

Features:

- Least expensive
- Durable
- Low energy density (disadvantage)
- Toxic.

→ Cell Notation:

$Pb, PbSO_4 \| H_2SO_4 | PbSO_4, \underbrace{PbO_2 | Pb}$

PbO_2 is pasted on Pb grid.

Recharging

- Low self discharge:
  - 40% in one year (3 months for NiCd).
- No memory
- Cannot be stored when discharged.
- Limited no. of full discharges.
- Danger of overheating during charging.

28/06/2022

* Ni–Cd Battery : Alkaline Battery (KOH)

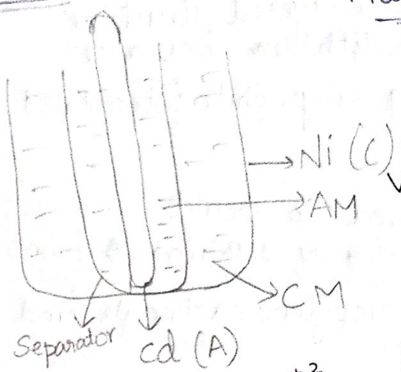
Anode: Cadmium (Cd)

Cathode: $Ni^{+3}O(OH)$

Separator: KOH

Anodic Material: Cadmium oxide, graphite, Cd, Fe (75–80%)

Cathodic Material: $NiO(OH)$ (80%), $Ni(OH)_2$, promoters + graphite pow



Voltage varies between 1·35–4

*A: $Cd^0 + 2OH^- \longrightarrow Cd^{+2}(OH)_2 + 2e^-$

*C: $NiO(OH) + 2e^- + H_2O \longrightarrow Ni(OH)_2 + 2OH^-$

$$NiO(OH) + Cd \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Ni(OH)_2 + Cd(OH)_2 + EE$$

- Used for moderate power drain out applications
- Compact batteries than lead acid.
- More reliable batteries and has more power density & energy density
- Toxic in nature (Cd)

$V = 1.4V$

- Used in electronic gadgets, flash lights, railways.

* Lithium-Ion Battery:

30/06/2022

- Secondary Battery
- Easy to form intercolated compounds b/w lithium ion and graphite.
- Anode and cathode are layered structure of graphite to which lithium ions are introduced forming Li-graphite intercolated compounds. [Li_xC]
- Electrolyte (solvent) to be used should facilitate the transfer of lithium from anode and cathode [propylene carbonate and ethylene carbonate]

* porous polypropylene ⇒ separator.

• Co, Mn → Cathodic Material (generally)

* Aluminium & copper foils are used as anode and cathode current collectors

* Reactions (DISCHARGE).

Anode:

$Li_xC \longrightarrow xLi^+ + xe^- + C$

LiMO$_x$: Lithium Transition metal oxide is used as cathode.

Cathode:

$LiCoO_2 + xLi^+ + xe^- \longrightarrow Li_{1+x}CoO_2$

temporarily Li enters the interstitial sites of graphite.

* $Li_xC + LiCoO_2 \longrightarrow Li_{1+x}CoO_2 + EE$

$\boxed{V = 3.5 \text{ to } 3.7\ V}$

- High capacity;
- High energy & power density.

* Binder: Poly vinylidene fluoride.

Lithium migration from

→ anode to cathode: discharging (e's:)
current is from cathode to anode.

→ cathode to anode: charging. (e's:)
current is from anode to cathode.

* Lithium Ion Recharging:

- 300 cycles
- 50% capacity at 500 cycles.

* Nickel-Metal Hydride Battery:

* Metal hydride (−) ; nickel oxy hydroxide (+)
* Potassium hydroxide aqueous electrolyte

$\boxed{V = 1.35V}$

- non-toxic

$KOH \longrightarrow K^+ + OH^-$

anode: $MH + OH^- \longrightarrow M + H_2O + e^-$

M : $LaNi_5$ or any alloy. which absorbs hyd

cathode:

$NiO(OH) + e^- + H_2O \longrightarrow Ni(OH)_2 + OH^-$

- capacity is high.
- Self discharge is very less, long shelf life in charged state.
- long cycle life.

01/07/2022

* FUEL CELLS: widely used in space stations

* Redox reaction ⇒ electrical energy.

⇒ Oxidising agent + Reducing Agent ⟶ Product + Electrical Energy

Oxidising agent: O_2/air

Reducing Agent (Fuel): H_2, CH_4, LPG, CNG, CH_3OH, C_2H_5OH.

Products formed are generally eco-friendly

Ex: Eco-friendly reaction:

$$\boxed{\underset{(RA)}{H_2} + \underset{(OA)}{O_2} \longrightarrow \text{Product}(H_2O) + E.E.}$$

⇒ CLASSIFICATION:

→ Working Temperature:

- → Low Temp. Fuel cell (<100°c).
- → Moderate Temp. Fuel Cell (150–200°c)
- → High Temp. Fuel cell (>500°c) ↓ (500°c to 650°c)

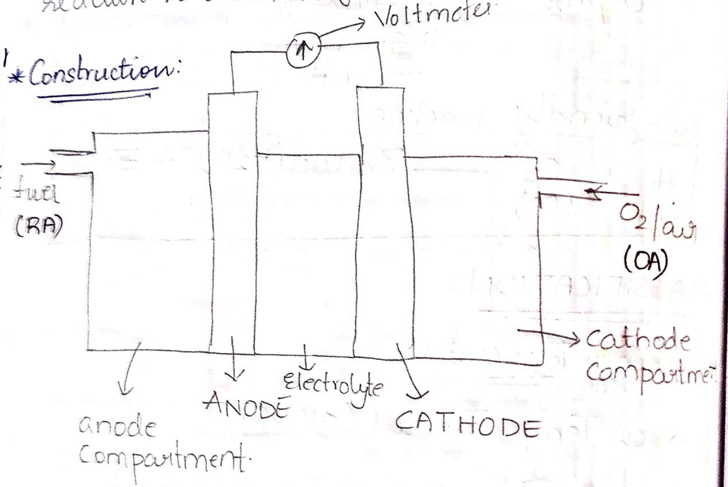
→ Materials and electrolytes:

- → Alkaline Fuel Cell (LTFC)
- → Phosphoric acid Fuel Cell (MTFC)
- → Moltencarbonate Fuel Cell (HTFC)
- → Bio-chemical Fuel Cell [LTFC]

→ Solid Oxide fuel cell [HTFC]
→ Polymer membrane electrolyte fuel cells. [MTFC]
↳ more efficient

* ⇒ Costly catalysts like Pt, Au are used in large amount to redox reaction to occur in fuel cells.

* **Construction:**



* Fuel and air/O_2 must be pumped in anode & cathode compartments respectively ∴ These are called flow batteries.

⇒
→ Methanol Oxygen F.C (low)
→ H_3PO_4 F.C. (moderate) → Commercial applications
→ Molten carbonate F.C (High).

04/07/2022.

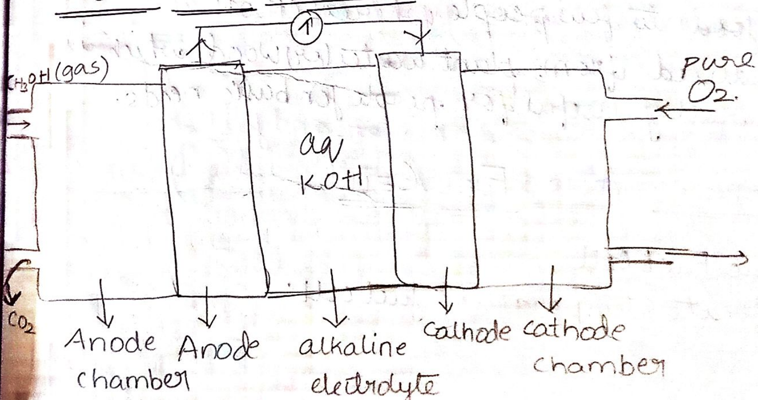
- Materials are less toxic.; – No noise.
- Multiple options due to selective fuels.
- High capacity (400MW approx).
- High efficiency

	F.C. Efficiency	+ Heat	Catalyst
* CH_3OH-O_2 F.C [low temp]:	40–45%		Ni, Rh, Pt, Pd
* H_3PO_4 – F.C (Moderate temp):	~50%	70–75%	Ni-Au, Ag.
* Molten carbonate F.C (high temp)	~45%	~70%	graphite rod Au, Ag

→ If the surface area of the catalyst is high, the efficiency is high.

→ H_3PO_4 fuel cell is preferred over other 2 fuel cells due to its moderate cost of the catalyst and efficiency is also quiet high.

* **CH_3OH-O_2 FUEL CELL: Alkaline Fuel Cell**



Catalyst = Pt/Pd & Ag.

* Redox reaction $\Longrightarrow$ Electrical Energy.

$KOH \longrightarrow K^+ + OH^-$

$\Rightarrow$ Anode:

$6OH^- + CH_3OH \xrightarrow{(O)} CO_2 + 5H_2O + 2e^-$

$\Rightarrow$ Cathode:

$\frac{3}{2}O_2 + 3H_2O \longrightarrow 6OH^{\ominus}$

$$\boxed{\frac{3}{2}O_2 + CH_3OH \longrightarrow CO_2 + 2H_2O + E.E}$$

* Products formed i.e. CO_2 is not dangerous compared to the products formed during burning the coal/petrol i.e. CO, SO_2, SO_3, NO_x

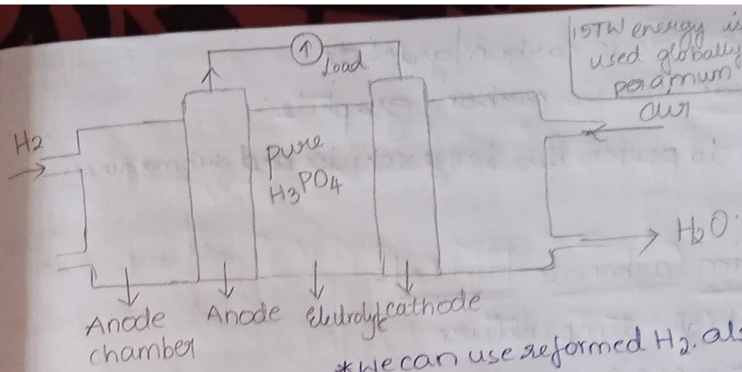
* C_2H_5OH is not used in this process because carbon percentage is more due to which % of CO_2 produced increases.

* Also C_2H_5OH is produced from food grains due to which ~~they~~ there will be no food to few people whereas CH_3OH is produced from plant wastes (or) wood which is not really useful for people for basic needs.

* PHOSPHORIC ACID FUEL CELL:

- Acidic Fuel cell
- Moderate temperature fuel cell.

15TW energy is used globally per annum



*we can use reformed H_2 also.

- Electrodes are made up of porous nickel.
- Anode: porous nickel impregnated with Pt group
- cathode: porous nickel coated with Ag. CH_3OH - O_2
- At low temp: H_3PO_4 freezes itself
  ∴ temperature should be $\geq 200°C$.

* Redox Reaction $\Longrightarrow$ Electrical Energy.

*→ Anode:

$2H_2 \longrightarrow 4H^+ + 4e^-$

*produces high E.E approx 400MW

*→ Cathode:

$O_2 + 4H^+ \longrightarrow 2H_2O$

$$\boxed{2H_2 + O_2 \longrightarrow 2H_2O + EE}$$

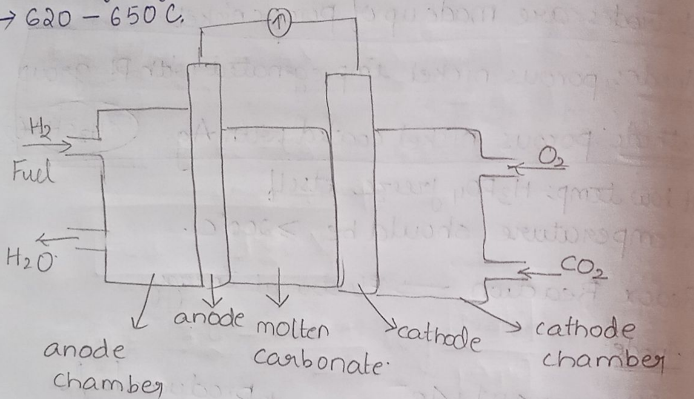
→ Electrolyte is highly concentrated or pure liquid H_3PO_4 saturated in a silicon carbide matrix.

* Electrodes are made of carbon paper coated with finely dispersed platinum (or) platinum group.

* At low temp: pure H_3PO_4 freezes itself.

Anode: Porous carbon/graphite.
Cathode: Porous carbon/graphite.
-used to power the large vehicles and submarines.

Molten Carbonate Fuel Cell:
↳ high temperature
→ 620 − 650°C.



Electrolyte: Na & K carbonates + $LiAlO_2$ (Lithium aluminate)

electrodes are made up of Nickel and chromium.

*Efficiency depending on heat and fuel cell i.e. 60−65%. ↳(very high)

*Anode: $H_2 + CO_3^{-2} \longrightarrow H_2O + CO_2 + 2e^-$

*Cathode: $2e^- + \frac{1}{2}O_2 + CO_2 \longrightarrow CO_3^{-2}$

$$\boxed{H_2 + \frac{1}{2}O_2 \longrightarrow H_2O + E.E}$$

*06/07/2022

→ Teflon, polyethene covers, bottle, brush, nylon clothes, rain coats, polyester clothes, umbrella, fibre glass, PVC pipes.

*08/07/2022

→ Concentration Cell Numericals:

$$\boxed{C_1 \neq C_2}$$

$$E = E^\circ - \frac{0.0591}{n} \log \frac{C_2}{C_1} \quad \begin{matrix} C_2 \rightarrow \text{cathode} \\ C_1 \rightarrow \text{anode} \end{matrix}$$

$\boxed{C_2 > C_1}$.

1) Concentration cell is constructed by placing 2 copper electrodes in 0.001 M and 0.1 M $CuSO_4$ solⁿs. These 2 half cells are connected by salt bridge. Calculate emf of the cell; cell notation & cell possible reaction.

$C_1 = 0.001M$ (anode) , $C_2 = 0.1M$ (cathode)

Cell Notation: $Cu/\underset{(C_1)}{Cu^{+2}}//\underset{(C_2)}{Cu^{+2}}/Cu$.

$Cu \longrightarrow \underset{(C_1)}{Cu^{+2}} + 2e^-$

$Cu^{+2} + 2e^- \longrightarrow Cu$.

$\underset{(C_2)}{Cu^{+2}} + Cu \longrightarrow \underset{(C_1)}{Cu^{+2}} + Cu$

$$E = \frac{-0.0591}{2} \log \frac{10^{-3}}{10^{-1}}$$

$$= \frac{-0.059}{2} \times -2$$

$$\boxed{E = +0.059\,V}$$

2) Calculate emf of the cell which has following reaction.

$$Mg + 2Ag^{+}(aq) \longrightarrow Mg^{+2}(aq) + 2Ag(s)$$

$[Mg^{+2}(aq)] = 0.001M$ and $[Ag^{+}(aq)] = 0.001M$

$E^{\circ}_{Mg/Mg^{+2}} = 2.4V$ $E^{\circ}_{Ag/Ag^{+}} = -0.80V$

$E^{\circ}_{Mg^{+2}/Mg} = -2.4V$ (Anode) $E^{\circ}_{Ag^{+}/Ag} = +0.80V$ (Cathode)

$E^{\circ}_{cell} = E_C - E_A$

$= +0.80 + 2.4$

$\boxed{E^{\circ}_{cell} = 3.20V}$

$E_{cell} = 3.2 - \frac{0.059}{2} \log \frac{[Mg^{+2}]}{[Ag^{+2}]^2}$

$= 3.2 - 0.0295 \log \frac{10^{-3}}{10^{-6}}$

$= 3.2 - 0.0295 \times 3$

$= 3.2 - 0.08865$

$\boxed{E_{cell} = 3.11135V}$

3) Can we use Copper container to store $AgNO_3$ (0.1M) solution at 25°C?

Can we use copper spatula to stir $AgNO_3$ solⁿ?

SRP of Cu = 0.34V Ag = 0.80V Write possible reaction.

$E_{cell} = E_C - E_A$

$= 0.80 - 0.34$

$= 0.46V$ (+ve)

$Cu^{\circ} + AgNO_3 \longrightarrow Ag^{\circ} + Cu(NO_3)_2$

The metal element which has higher SRP value should be in 0 state to avoid any reaction.

If it is in higher oxidation state ; reaction takes place

4) Can we use Mg container to store $ZnSO_4$?

Can we fit Mg tap to withdraw $ZnSO_4$?

SRP value of Mg = −2.4V and Zn = 0.76V

Zn is having higher SRP value ∵ it is in +2 state ∴ Reaction takes place.

∴ We cannot use Mg container to store $ZnSO_4$.

5) Determine the pH of solution using Quinhydrone electrode.

6) Any one electrode, electrode notation, reaction and Nernst equation, advantages & disadvantages.