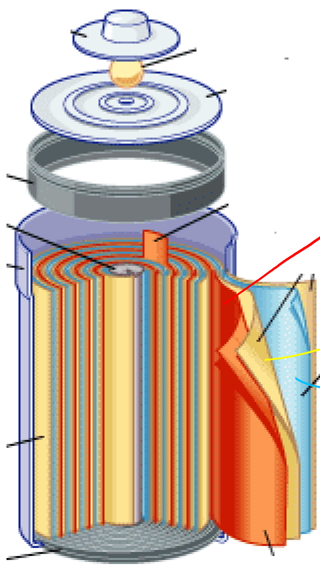
Secondary Cells.

Ni – Cd Cells



Cd/CdO → anode

Porous material Soaked with Sat. KOH

NiO(OH)/Ni → Cathode

Electrolyte : Sat. KOH
anode : CdO/Cd
Cathode : NiO(OH)/Ni
Max Voltage : 1.4 V

Cell representation :-

$$Cd_{(s)}/CdO_{(s)}/KOH//NiO(OH)_{(s)}/Ni_{(s)}$$

reaction :-

Discharging :-

@ anode

$$1 \times \quad Cd \longrightarrow Cd^{2+} + 2e^-$$

@ Cathode

$$2 \times \quad NiO(OH) + e^- + H_2O \rightarrow Ni(OH)_2 + OH^-$$

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

overall reaction

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

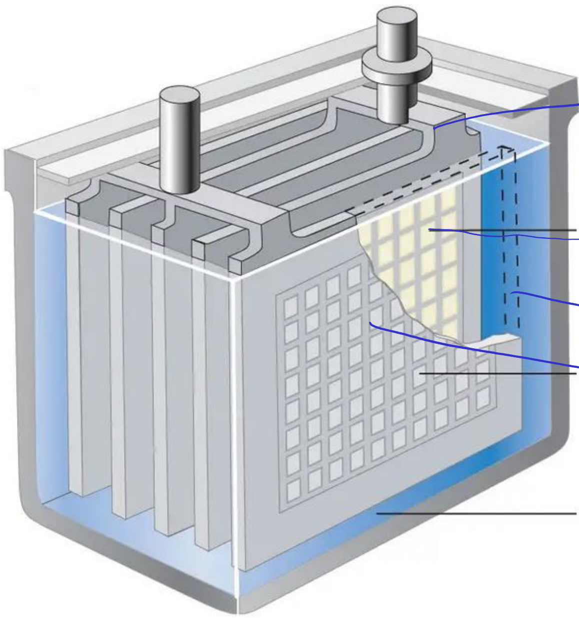
$$Cd(OH)_2 \rightarrow CdO + H_2O$$

$$Cd + 2NiO(OH) + H_2O \longrightarrow CdO + 2Ni(OH)_2$$

During recharge

$$CdO + 2Ni(OH)_2$$
$$\downarrow$$
$$Cd + 2NiO(OH) + H_2O$$

Lead-Acid cell



Pb alloy

Spongy Pb

35% H_2SO_4

PbO_2

anode: spongy lead
Cathode: PbO_2
electrolyte: 35% H_2SO_4
Max. output: 2V

Representation

Pb alloy / Pb / H_2SO_4 / PbO_2 / Pb alloy

While Discharging

@ anode

$$Pb \rightarrow Pb^{2+} + 2e^-$$

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

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

@ Cathode

$$PbO_2 + 2e^- + 4H^+ \rightarrow Pb^{2+} + 2H_2O$$

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

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$$

Overall reaction

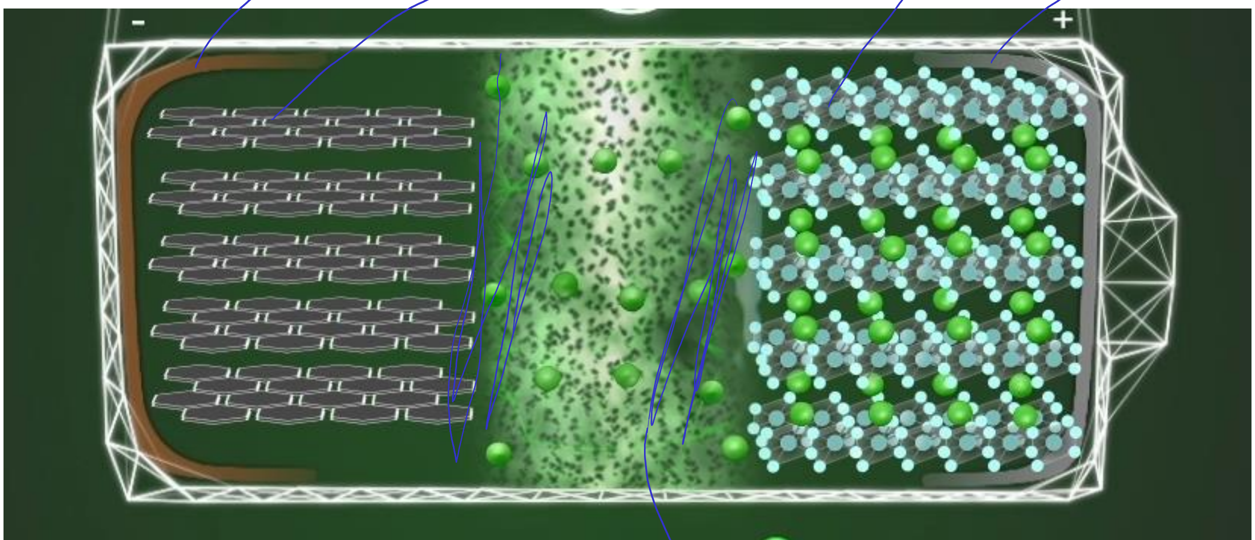
$$Pb + 2SO_4^{2-} + PbO_2 + 4H^+ \rightarrow 2PbSO_4 + 2H_2O$$

$$\boxed{Pb + 2H_2SO_4 + PbO_2 \rightarrow 2PbSO_4 + 2H_2O}$$

While Charging

$$2PbSO_4 + 2H_2O \rightarrow Pb + 2H_2SO_4 + PbO_2$$

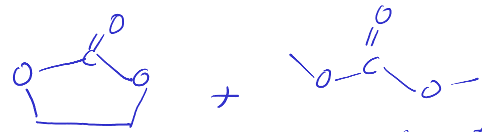
Lithium ion cell



anode :- graphite / Cu metal

Cathode : $LiCoO_2$ / Al

Electrolyte : Ethyl carbonate,
dimethyl carbonate,
$Li^+[P(F_6)]^-$



Ethyl Carbonate + dimethyl Carbonate

+

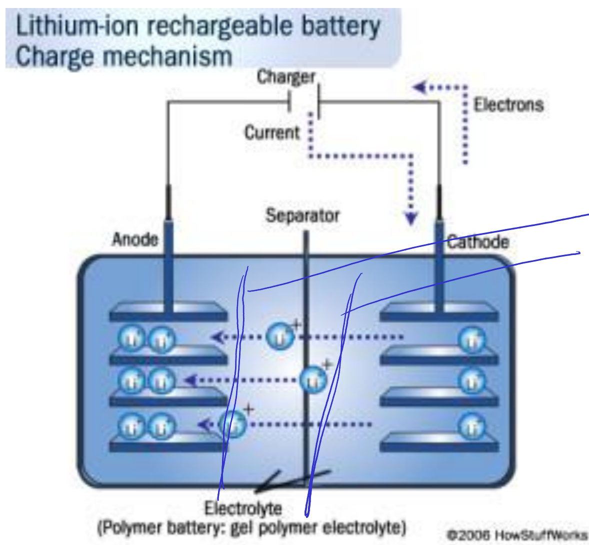
$Li^+[P(F_6)]^-$

→ Cell functions by Conducting Li ions from one electrode to another electrode

→ Ethyl Carbonate, dimethyl Carbonate

→ Li salt Used to ensure rapid transfer of Li^+ from one electrode to another electrode

→ When cell started working the electrolyte undergo electrolytic decompositions to form
- Solid electrolyte interface



anode solid electrolyte interface

cathode solid electrolyte interface

↓

help the Li^+ ion to intercalate

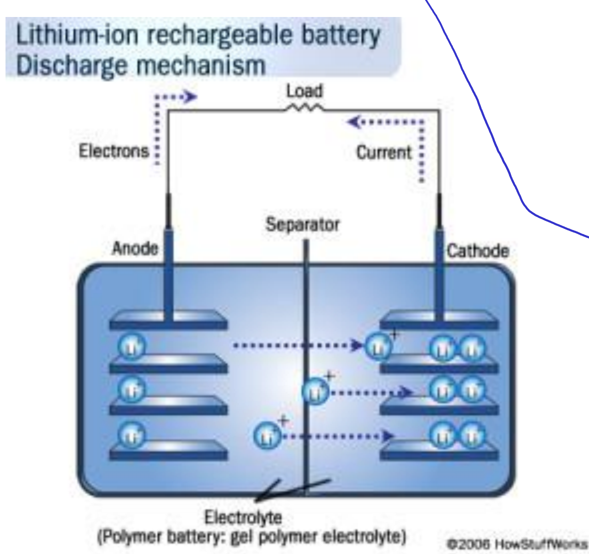
@ anode

$$C_6 + Li^+ + 1e^- \rightarrow Li^+C_6^-$$

@ Cathode :-

$$LiCoO_2 \rightarrow CoO_2 + Li^+ + 1e^-$$

$$LiCoO_2 + C_6 \rightarrow LiC_6 + CoO_2$$



$$CoO_2 + LiC_6 \rightarrow C_6 + LiCoO_2$$

While Discharging

$$\text{Anode} \xrightarrow{Li} \text{Cathode}$$

While Charging

$$\text{Cathode} \xrightarrow{Li} \text{anode}$$

Fuel cells / Flow cells

Fuel ⟶ Electricity

↓ Burn   Traditional method

Heat $\xrightarrow{H_2O}$ Super heated Steam ⟶ turns turbaine ⟶ turns Electricity generator

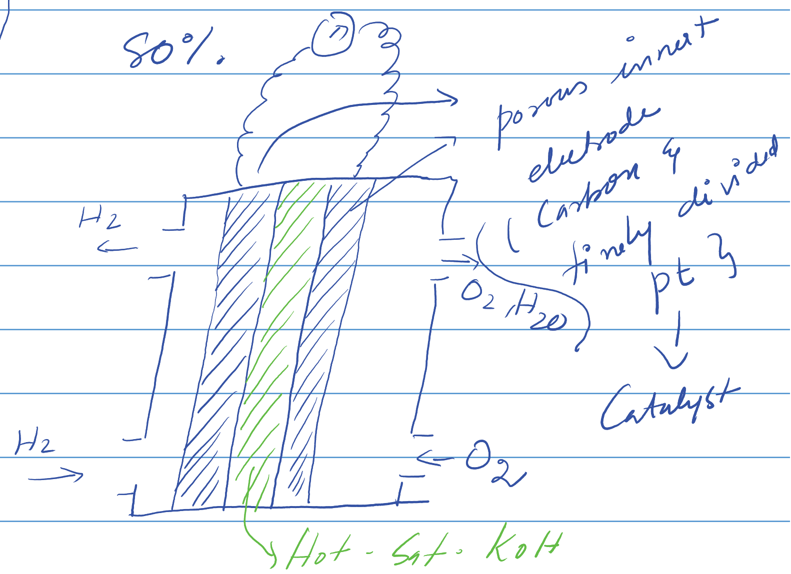
efficiency → 40%

fuel cell

Fuel ⟶ Fuel cell ⟶ electricity

80%

Hydrogen fuel cell



electrode: Carbon electrode

fuels: H_2 & O_2

Electrolyte: KOH

Catalyst: Pt

Max. vnt: 1.2V

@ anode:-

$$H_2 \rightarrow 2H^+ + 2e^-$$
$$2H^+ + 2OH^- \rightarrow 2H_2O$$
$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \quad \text{—(1)}$$

@ Cathode

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad \text{—(2)}$$

Overall reaction is (1)+(2)

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

Hydrogen - PEM Cell

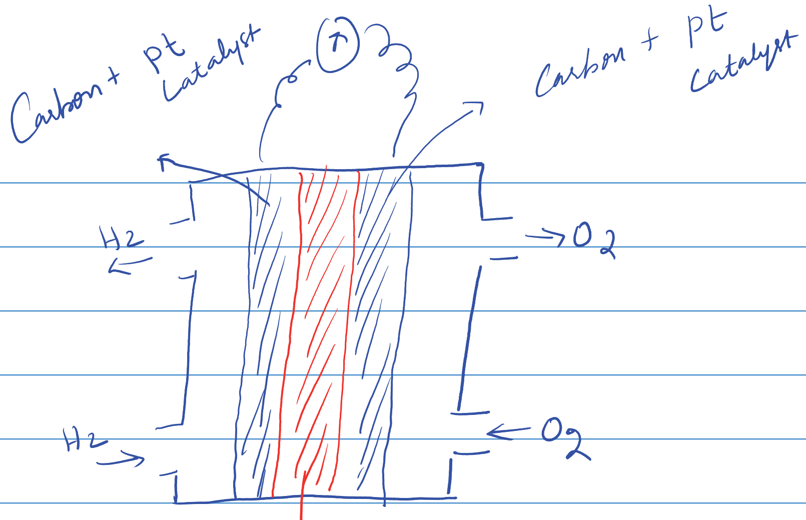
@ anode

$$H_2 \rightarrow 2H^+ + 2e^-$$

@ Cathode

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

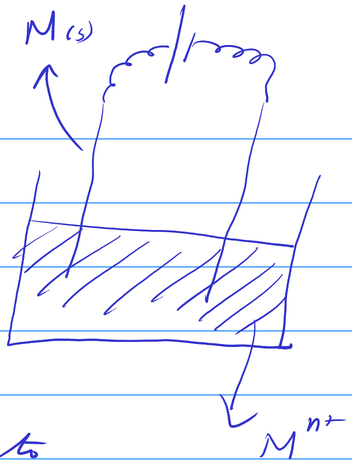
$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$



Proton exchange membrane (PEM)

it allows only H^+ to pass through

Electroplating



@ anode

$$M_{(s)} \longrightarrow M^{n+} + ne^-$$

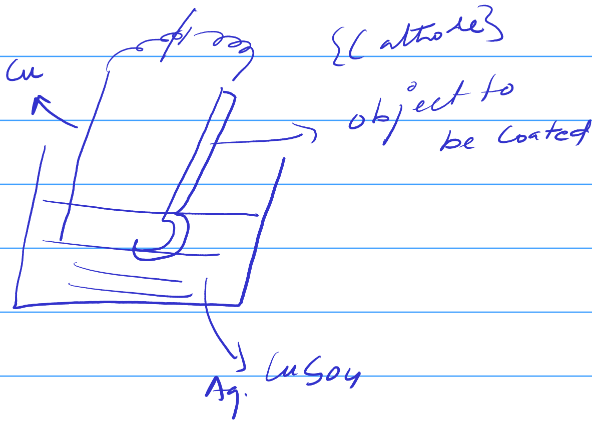
@ Cathode

$$M^{n+} + ne^- \longrightarrow M_{(s)}$$

Electrolyte - Aq. Salt of metal to be coated

anode - pure metal of metal ion in the electrolyte

Cathode → Object to be coated



if we want to Coat Cu

@ anode

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

@ Cathode

$$Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$$

Theory of electroplating

faraday found
→ amount of substance liberated / deposited at the electrod during electrolysis depends on

1. Quantity of Current passed
2. time duration of Current passed @ uniform rate
3. Charge on the ion being deposited

faraday's law : I

$$W \propto Q$$

Amount of Substance deposited / liberated

Quantity of electric Charge

$$Q = I \times t$$

I → Current in amp (C/s)

t → time in 'sec'

$$W \propto I \times t$$

$$W = z I t$$

W → Amount of Substance deposited

z → Proportionality Constant (electrochemical equivalent) → it is a Characteristic of Substance deposited

I → Current

t → time

If

$I = 1$ amp & $t = 1$ sec

then

$$W = z$$

electrochemical equivalent → amount of Substance deposited when 1 amp of Current passed 1 sec.

$$\text{Unit of } z = \frac{W}{I \times t} = \frac{kg}{\frac{C}{\cancel{s}} \times \cancel{s}} = \frac{kg}{C}$$

(W → kg, I → C/s, t → s)

for a large Quantity of Current let us Say

$1\,F \rightarrow 96500\,C$

If we pass 1 F of Current for 1s then amount of Substance deposited is Called as 'Equivalent Weight (or) gram Chemical equivalent'

"Z"

electrochemical equivalent

$E = Z \times 96500 \times 1$

equivalent weight

$Z = \frac{E}{96500}$ → equivalent weight.

$E = \frac{\text{Molecular Wt}}{\text{Valancy}}$

electrochemical equivalent $(Z) = \frac{\text{Molecular Wt}}{\text{Valancy} \times 96500}$

We Know

$W = Z \times I \times t$

$$\boxed{W = \frac{\text{Molecular Wt.}}{\text{Valancy} \times 96500} \times I \times t}$$

current (amp)

time (s)

Eg:1

How many amp of current must be passed through a cell to produce Na metal at the rate of 30 Kg/h

$W = \frac{MW}{V \times 96500} \times I \times t$

$t = 1 \times 60 \times 60 = 3600s$

$W = 30$ kg

$Z = \frac{23 \times 10^{-3} \text{ kg}}{1 \times 96500} = 2.38 \times 10^{-7}$ kg/c

$$I = \frac{W}{Z \times t} = \frac{30\ (kg)}{2.38 \times 10^{-7}\ (kg/c) \times 3600\ (s)}$$

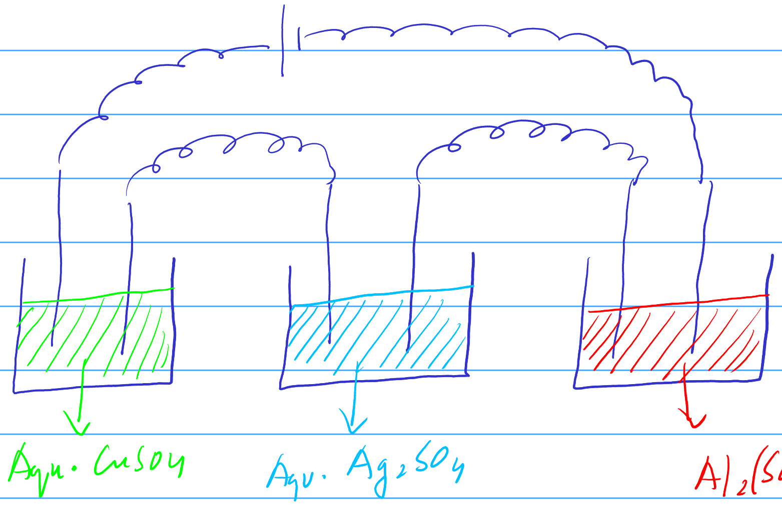
$$= 34{,}963\ (C/s) \leftrightarrow amp$$

Significance:-

we Can identify electrochemical equivalent

Faraday's II law

Same amount of electricity is passed through different electrolyte, the amount of Substance deposited is proportional to equivalent weight



if 1 Faraday of Current is passeded for 1 sec

$Cu \rightarrow \frac{63}{2} = 31.5$ gm

$Ag = \frac{108}{1} = 108$ gm

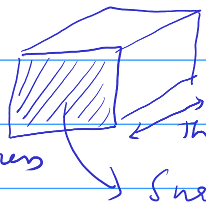
$Al = \frac{27}{3} = 9$ gm

equivalent wt $\Rightarrow$ amount of Substance deposited when 1 F of Current passed fo 1 sec

Thickness of plating :-

Density = gm/ml $\Rightarrow$ Weight/Volume

Volume = Surface Area × Thickness



$$\text{Density} = \frac{\text{Weight}}{\text{Surface area} \times \text{Thickness}}$$

$$\text{Thickness} = \frac{\text{Weight}}{\text{Surface area} \times \text{Density}}$$

We know

$$\text{Weight } (w) = \frac{M.W}{\text{Valancy} \times 96500} \times I \times t$$

$$\text{Thickness} = \frac{M.W \times I \times t}{\text{Valancy} \times 96500 \times \text{Surface area} \times \text{Density}}$$

eg:

Calculate the thickness of 'Ni' plated on to the object having surface area of 22 cm^2, if we pass 1.5 amp of current for 1.5 hr.

given: Density of Ni = 8.9 gm/cm^3
Mw : 58.7

$t = 1.5 \times 60 \times 60 = 5400\,s$

$$w = \frac{1.5 \times 5400 \times 58.7}{2 \times 96500} = 2.46\,gm$$

$$T = \frac{W}{D \times SA} = \frac{2.46\ (gm)}{8.9\ (g/cm^3) \times 22\ (cm^2)} = 0.0126\ cm$$

eg :-

Calculate the thickness of Ni plated on to the Surface area of 22 cm^2, if we pass 1.25 amp of Current for 1.5 hrs. Density of Ni = 8.9 gm/cm^3 & MW = 58.7

$$W = \frac{58.7}{2 \times 96500} \times 1.25 \times (1.5 \times 60 \times 60)$$

$$= 2.05 \text{ gm}$$

$$T = \frac{W}{D \times SA} = \frac{2.05}{8.9 \times 22} = 10.5 \times 10^{-3} \text{ cm}$$

Current efficiency :-

$$W \propto Q$$

$$\text{Current efficiency} = \frac{\text{Weight of the metal deposite}}{\text{theoritical weight to be deposited}} \times 100$$