UNIT 3

Battery Technology

- Battery converts chemical to electrical energy
- Battery is a device that stores chemical energy and on demand, converts it into electrical energ

Why we use batteries

(1) Portable sources of energy
(2) Come in various shapes and sizes
  - smallest battery: hearing aid.
  - submarine battery: 200 tonnes

To construct battery (galvanic cell)

(1) Anode material
  - something that oxidises easily
  - usually, metals (Zn, Li etc.)

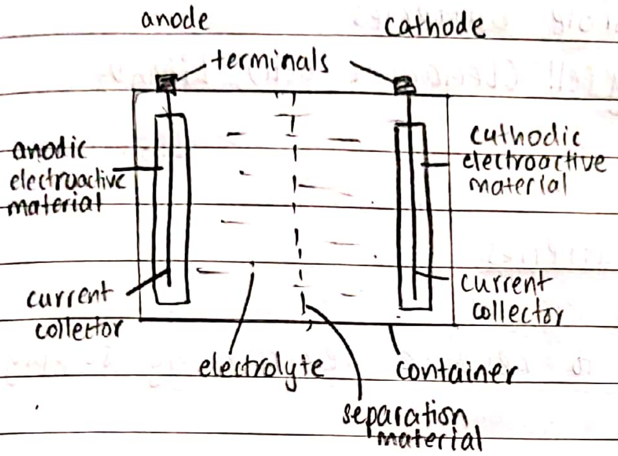
(2) Cathode material
  - substant that reduces easily
  - usually, oxide of metal or compound of metal, O_2 (electroactive species, not conductor ~~if required, we need a current collector~~

(3) Electrolyte
  - acid, alkali or salt solutions
  - nowadays, even solid electrolytes are used.

(4) Separator
  - separates anode compartment from cathode compoment
  - allows movement of ions

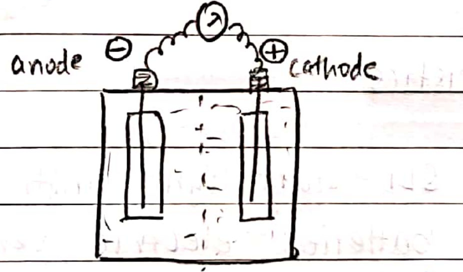
- prevents short-circuiting
- vinyl polymers, cellophane, muslin cloth

WORKING OF A BATTERY



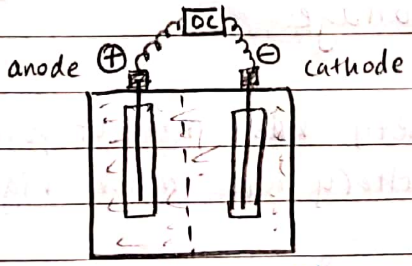
energetically not favorable for e^- to move through electrolyte

Discharging power (Galvanic cell)



$M \rightarrow M^{n+} + ne^-$ $A + ne^- \longrightarrow A^{n-}$

Charging (electrolytic cell)



- regenerated electroactive species

$A^{n-} \longrightarrow A + ne^-$ $M^{n+} + ne^- \longrightarrow M$

Classification of Batteries

(1) Primary batteries

- one-time use
- irreversible batteries
- eg: dry cell (Leclanche cell), $LiMnO_2$

(2) Secondary batteries

- possible to reverse reaction by supplying current
- regenerates electroactive species
- reversible batteries / storage batteries
- eg: Pb-acid battery, Li-ion, Ni-Cd batteries
  (Cd) hazardous; water bodies

Battery characteristics

- Car batteries: SLI - start, light, ignition (Pb-acid); car traction batteries - electric vehicle
- Pb-acid not used for car batteries; Li-ion batteries.
- Demand for each battery very different.
- Pb-acid: powerful for short period of time (~6 M H_2SO_4)
  Li-ion: steady voltage

- Pacemaker battery has mW of power requirement whereas car battery has much higher power requirement.

(1) Voltage

- emf of the cell - obtained from free energy change - depends on reaction - choice of electrode
- $E = E^0 - \frac{2.303RT}{nF} \log Q$

Factors on which Voltage depends on:

(a) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ (choice of electrodes)

(b) Temperature

(c) Q - reaction quotient - extent of reaction

$$Q = \frac{[products]}{[reactants]}$$

effect of Q not as much due to it being a log term.

$\therefore E_{cell}$ is very close to E°_{cell}.

- as rxn proceeds, Q changes
- battery still gives steady voltage
- dry cell ~1.5V steady as listed, until cutoff point
- if T increases, E should decrease
- but keeping batteries in the sun would get the rxn to start again; kinetics

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(2) Current

- current is the rate at which the battery is discharging. (rate at which e^- are generated; kinetics)
- rapid electron transfer reaction

For rapid electron transfer reaction:

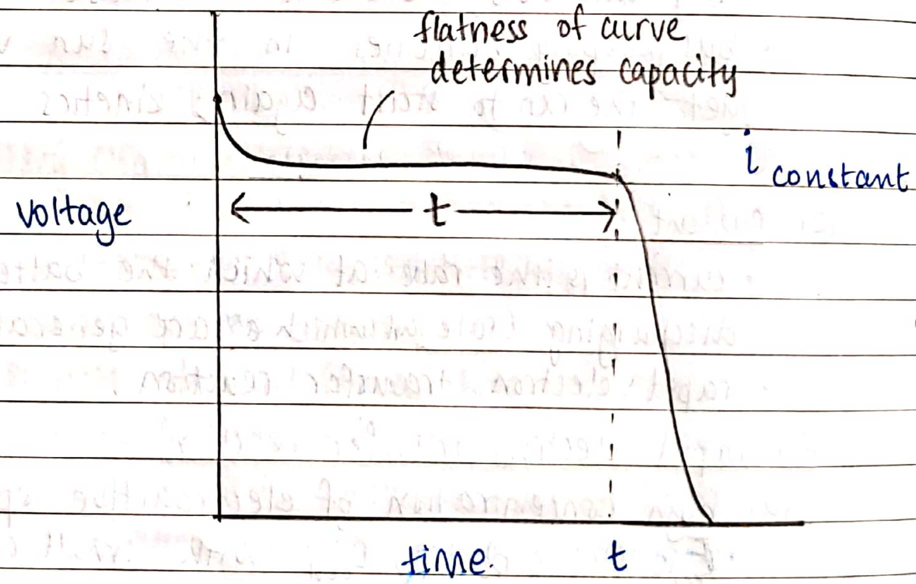
(a) high concentration of electroactive species
- E_{cell} is still close to E°_{cell} with small conc.
- bulb flickers because current cannot be drawn; E_{cell} is ~ same

(b) highly conducting electrolyte
- if electrolyte offers resistance, I_{max} is less

(c) reduce interelectrode distance
- $R \propto l$

(3) Capacity

- it is the charge or amount of electricity that can be obtained from the battery
- depends on the size of the battery
- common unit – Ah, mAh
- $\boxed{C = \frac{wnF}{M}}$ w = weight of electroactive specie
  n = no. of electrons
  F = Faraday's constant
  M = molar mass of electroactive species.
- listed capacity: the lower capacity
- AA and AAA both 1.5 V; only capacity different (size of battery different).



- Capacity is given by the current drawn over a period of time (cutoff time)
- Time for which battery lasts.
- $\boxed{C = i \times t}$
- length of time determines capacity.
- Capacity also depends on discharge conditions.
- Short circuit: i so high that t is small; battery die

(4) Electricity storage density

- Lead-acid battery for car – 50Ah; for industrial use – 1000Ah.
- Voltage is still ~2V; constant
- UPS needs to last 1 hour

- it is a measure of charge per unit weight stored in the battery = capacity/weight
- weight of entire battery (both species + terminals + case + electrolyte)
- good electricity storage density ⇒ good battery design, lightweight battery.

- ∴ Li is a very popular anodic material
- 7g of Li gives 1F of charge, whereas $\frac{208}{2}$ = 104 g of Pb gives 1F of charge.

For 1 F of charge

Li	7g	(7/1)
Pb	104g	(208/2)
Al	9g	(27/3)
Mg	12g	(24/2)

(5) Cycle life of battery

- only for secondary batteries
- number of charge-discharge cycles that are possible before failure occurs.
- does not allow endless charging-discharging

Reasons for failure:

(a) Corrosion of contact points (acid, alkali, salt solution, metal)

(b) shedding of active material (instead of depositing on electrode/current collecter, sheds down; not available for further use)

(c) Morphological changes (expect uniform deposition, dendrites form)

- if anode & cathode come in contact due to dendrites, circuit is shorted
- can pierce through separator

- that is why we should ~~completely~~ discharge before charging to a decent amount
- repeated charging is damaging; does not form layers properly
- should not fully discharge it (electrolyte in contact with current collector)
- memory effect : due to crystal formation

???
- Cellphone batteries:

- Should NEVER overcharge batteries.
- electroactive species should be regenerated
- if Pb-acid battery is overcharged, H_2O gets electrolysed and H_2 and O_2 are liberated, causing an explosion.
- Now, maintenance-free battery; overcharging forms H_2 and O_2 $\xrightarrow{\text{recombine}}$ H_2O with catalyst.

- Jumpstart: sudden surge of power electroactive species may get overcharged & H_2O may electolyse, causing explosion.

- while charging & discharging at the same time (mobile phones), battery is charging and we are using power directly from source, not from battery
- Battery cannot act as both galvanic and electrolytic cell at the same time.

(6) Energy efficiency

- % energy efficiency = $\frac{\text{energy released during discharge}}{\text{energy required during charge}}$
- is expressed in %
- depends on electrode reactions
- only to secondary batteries

(7) Shelf-life

- duration for which a battery can be stored without being used and yet give a specified performance.
- self-discharge, corrosion, secondary reactions
- secondary reactions occur very slowly
- very important for primary battery ; dies
- for secondary batteries, can be recharged
- Old batteries (Li ion) needed to be charged for 8 hours
- pacemaker batteries – 6 to 8 years (primary battery), $Li-I_2$ cell used

(8) Tolerance to Service conditions

- car batteries need to withstand terrain, temperature
- pacemaker batteries – 37°c

(9) Power Density

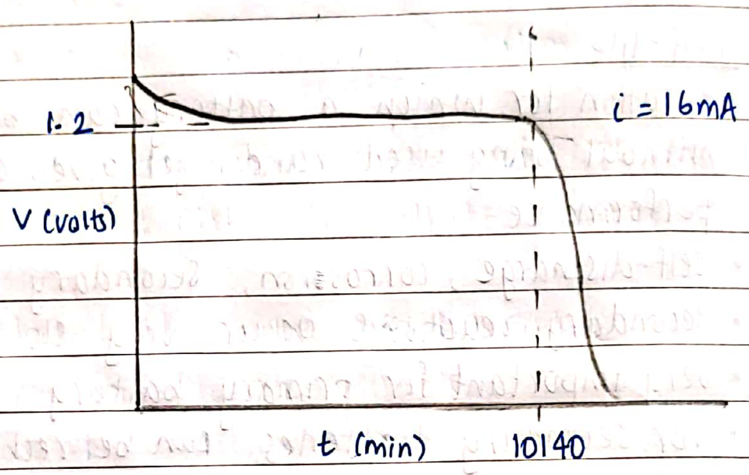
- ratio of the power available from a battery to its weight.
- $\frac{i \times E}{W}$ $W\,kg^{-1}$ = Power density

(10) Energy density

- the energy obtainable per unit weight of the battery
- $E \cdot D = \frac{i \times E \times t}{W}$ [illegible] $Wh\,kg^{-1}$

Q1: A battery-operated radio using AA size battery (MnO_2) weighing 50g. If the radio drains 16mA at 1.2 V, it lasts for 10140 minutes (i) Represent this data on a voltage-time graph. (ii) Calculate capacity, power density, energy density, electricity storage density.

(i)



(ii) $C = i \times t = (16\ mA)(10140 \times 60\ s)$

$= 9734\ C = 2.704\ Ah$

$P.D = \frac{i \times E}{W} = \frac{(16\ mA)(1.2\ V)}{(50 g)} = \frac{(16)(1.2)(\cancel{10^{-3}})}{(50)(\cancel{10^{-3}})}$

$= 0.384\ W\ kg^{-1}$

capacity / unit wt.

$E.D = P.D \times t = 0.384 \times 10140 \times 60$

$= 233.6\ kJ\ kg^{-1}$

$= 64.896\ Wh\ kg^{-1}$

$ESD = \frac{9734}{50} \times 10^3\ C kg^{-1} = 194.68\ kC\ kg^{-1}$

Q2: Pb-acid battery uses 150g Pb as anode material.
(i) Find out capacity of the battery (Ah)
(ii) If it gives V = 1.9V, what is the energy stored inside the battery? (Wh)
(iii) If battery weighs 1200g, lasts for 600 mins, for constant current i, find P.D.

$$Pb \longrightarrow Pb^{2+} + 2e^- \qquad M_{Pb} = 208\ g.$$

(i) $$C = \frac{nFW}{M} = \frac{(2)(96500)(150)(\cancel{10^{-3}})}{(208)\ (\cancel{10^{-3}})}$$

$= 139182.7$ A S

$C = 38.66$ Ah

(ii) $V = 1.9\ V$; $E_n = 38.66 \times 1.9$

Energy = 73.46 Wh

(iii) $$P.D = \frac{\text{energy (total)}}{\text{time} \times \text{weight of battery}}$$

$$= \frac{73.46\ Wh}{\left(\frac{600}{60}\ h\right) \times (1.2\ kg)} = \frac{73.46}{12}$$

$= 6.12\ W\,kg^{-1}$

MODERN BATTERIES

- dry cell - not heavy duty, not rechargeable
- Pb-acid battery - solved shortcomings of dry cell
- Pb-acid batteries are bulky
- capacity depends on H_2SO_4 amount (all electroactive species)
- can never be made small

- Ni-cd batteries: button-sized, rechargeable
- cd toxic; effluents pollute water near factories

- replaced cd with metal hydride
- tested for electric vehicles

(1) zinc-air battery

Class: metal-air battery (CO_2)
alkaline battery

- electrolyte - alkali
- anode: Zn
- cathode: O_2 (from atmosphere)

- cathode active material need not be stored inside the battery
- energy density very high (low weight)
- battery can be miniaturised

Construction.

(i) Anode

- Zn is taken as granules — more surface area
- Zn granules + gelling agent (to hold granules) + small amt. of electrolyte

(ii) Cathode

- need a current collector for any cathode active material.

C + catalyst (MnO_2 mixture) + wet proofing agent coated on a Ni mesh with an outer gas permeable Teflon layer

acts as a waterproof boundary — layer

- O_2 reduction is a slow process
- Therefore, we need a catalyst (MnO_2) to speed up the reduction of O_2.

- Water proofing to prevent moisture from entering

- Current collector – Ni mesh

- Teflon is permeable to gas, but is water proof.

(iii) Electrolyte

- alkali

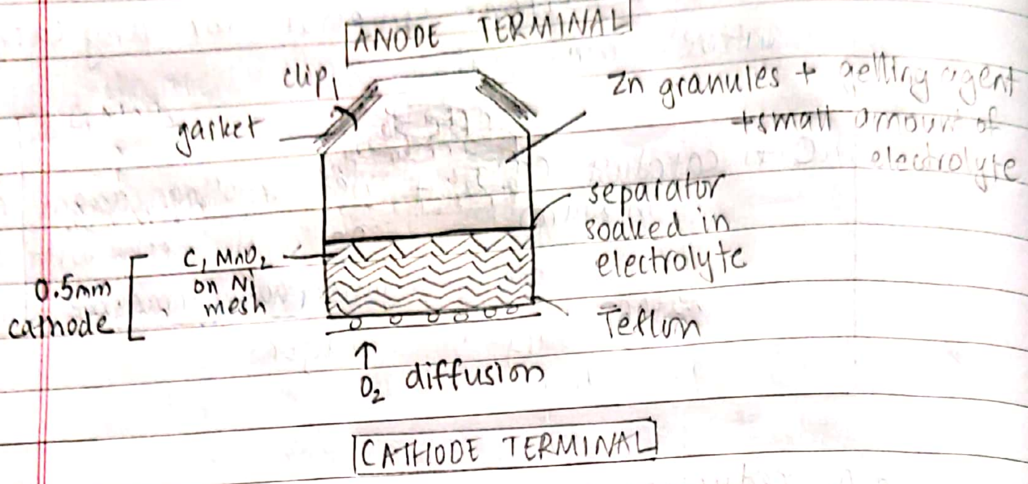
30% KOH or 5M NaOH

- moisture will interfere with concentration.

(iv) Separator

polypropyline soaked in electrolyte

Diagram



- gasket to insulate anode from cathode

Working (discharging)

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

$\underline{Zn^{2+} + 2OH^- \longrightarrow ZnO + H_2O}$

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

Cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Cell reaction: $Zn + \frac{1}{2}O_2 \longrightarrow ZnO$

- reaction is like a combustion reaction
- electrolyte not figuring in final reaction
- amount of electrolyte in battery not important

- separator soaked in electrolyte is sufficient
- can be made very small - used in hearing aids

- can be <u>miniaturised</u>

- High capacity (cathode is very thin): anode active species can fill up battery
- O_2 taken from atmosphere.
- Capacity depends only on amount of Zn in battery.

- shelf life almost unlimited (very, very long)
- sealed batteries are cut off from atmosphere
- almost no self-discharge

- Primary battery
- reaction cannot be reversed inside cell.
- Can collect ZnO and retrieve Zn from external method, easily reducable.
- non-rechargeable, but recyclable

- emf: 1.4 V generated
- sufficient for hearing aid.

Advantages

1. High energy density
2. No ecological problems (unlike Cd)
3. Low-cost (Zn is cheap)

Disadvantage

1. Can be easily poisoned by other gases. (dependent on environmental conditions)

$$KOH + CO_2 \longrightarrow KHCO_3 \longrightarrow K_2CO_3$$

brings down efficiency

Applications

1. Hearing aids
2. Voice transmitters
3. Railroad signalling

(2) Lithium Batteries

- Electric vehicles, mobile phones, laptops

(a) Why is Li such a popular anodic material?
- Li is the lightest metal (7g — 1 F of charge)
  ∴ has high energy density.

- Very -ve reduction potential (−3.05 V)
  ∴ undergoes Oxidation very easily.

- High output voltage due to the E° value
  (~4V in most cells).

(b) Li - anode material
cathode:
- MnO_2
- SO_2Cl_2 (sulphonyl chloride)

electrolyte:
- $LiClO_4$ in organic solvents (perchlorate), polymer batteries
- Li conducting PEO (polyethylene oxide)

(c) Aqueous electrolyte should not be used.

- Li explodes in H_2O due to rigorous reaction between Li and H_2O.

- Common solvents: CH_3COCN (acetonitrile), ethylene carbonate.

- Organic solvents are non-conducting

- complex salt usually dissolved in organic solvents
- common salts: $LiClO_4$, $LiPF_6$
- Inorganic solvents: SO_2Cl_2 , $SOCl_2$

(d) Li batteries can be primary or secondary

Primary — $LiMnO_2$ — long term memory backup.
Secondary – Li-ion

- clock runs when computer is off
- $Li-MnO_2$ battery (4-5 years)
- long-term memory backup.

Advantages & Disadvantages

Advantages.
- High cell voltage (~4.0 V) due to large -ve E°_{red}.
- High energy density due to low atomic mass of Li
- Operates over a wide range of temperatures (-40°C to 70°C)
- Shows flat discharge characteristics (gives steady voltage)

Disadvantages
- Not safe due to high reactivity
- Poor cycle life (dendrite formation very common); Li dendrite formation takes place which leads to short circuiting ⇒ could lead to explosion.
- Transportation limits (IATA) pure Li - < 8g , Li-ion batteries - < 99 Wh only in carry on to prevent self-activation.

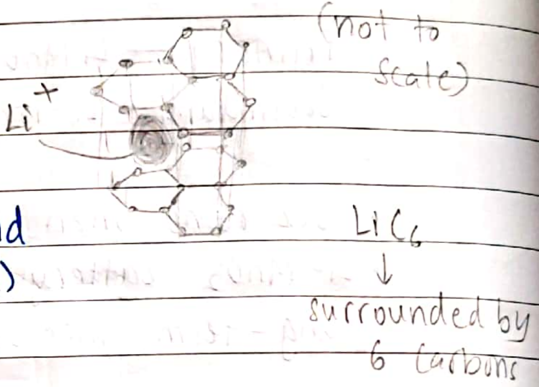
(3) Li-ion batteries (Nobel prize 2019)

- first battery — Sony 1991
- only Li ion
- anode - graphite (Li^+ can fit between layers)
  cathode - $LiCoO_2$ (Li^+ can fit in spaces)
- when battery made, it is in complete discharge.

Construction

(i) Anode

- Lithiated graphite intercalation compound pasted on Cu (plate)



(ii) Cathode

- metal oxide containing Li ($LiCoO_2$) pasted on Al (plate)

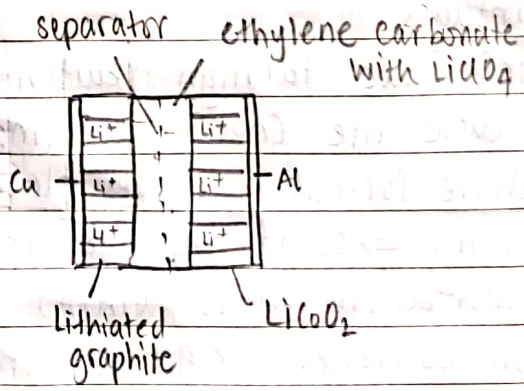
(iii) Electrolyte

- ethylene carbonate with small amount of $LiClO_4$

(iv) Separator

- polypropylene

Diagram



(needs to charge first and obtain Li^+ from cathode)

Working - Discharging

Anode: $x LiC_6 \longrightarrow xLi^+ + xe^- + xC_6$

Cathode: $Li_{(1-x)}\overset{+4}{Co}O_2 + xLi^+ + xe^- \longrightarrow Li\overset{+3}{Co}O_2$

- Li^+ does not take up e^- (while charging) at anode; C becomes slightly -ve.
- Lithiated Carbon has similar E° to Li
- E° value of Lithiated Carbon is not due to oxidation of Li
- $E_{cell} = 3.6 V$
- There is no Li in the battery at all, only Li^+

Cell reaction:

$$xLiC_6 + Li_{(1-x)}CoO_2 \longrightarrow xC_6 + LiCoO_2$$

~~Dis~~Charging

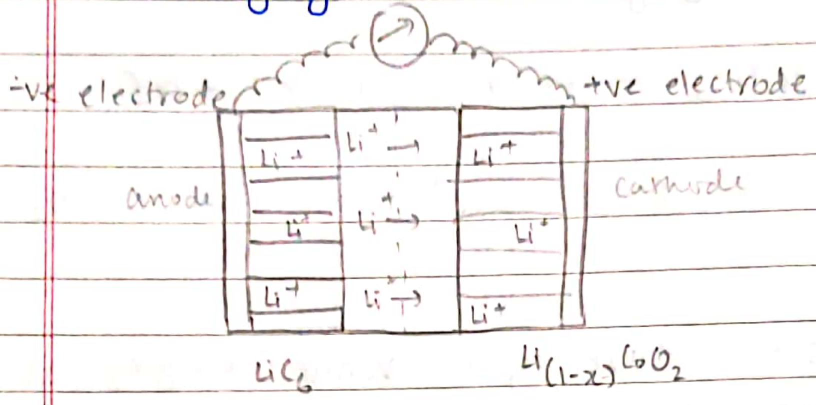
Anode: $LiCoO_2 \longrightarrow Li_{(1-x)}CoO_2 + xLi^+ + xe^-$

Cathode: $xC_6 + xe^- + xLi^+ \longrightarrow xLiC_6$

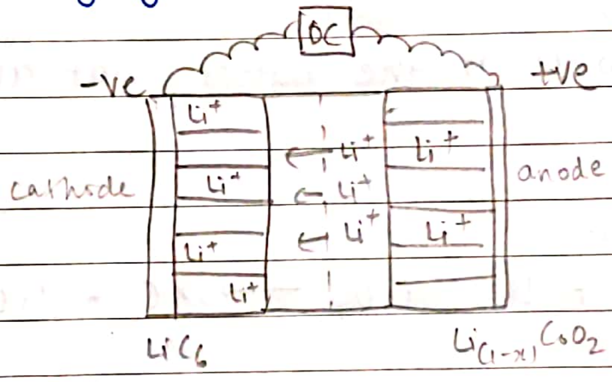
cell reaction:

$$LiCoO_2 + xC_6 \longrightarrow Li_{(1-x)}CoO_2 + xLiC_6$$

Discharging



Charging



Advantages of Li-ion Battery

1. High voltage
2. High energy density
3. Good cycle life (no dendrite formation)
4. No memory effect (unlike Ni-Cd effect)
5. Self-discharge is low compared to Ni-Cd and Ni-H
6. Temperature range (-40° to 70° c)
7. Safe to use (no Li metal present during charging or discharging.

~~Discharg~~

- Temperature controller to ensure that organic solvent does not catch fire

Disadvantage of Li-ion Battery

1. Organic solvent is inflammable; not that safe

- Polymers are used; high resistance
- Polymers should conduct Li^+

- Battery swells up with time
- Should not constantly charge/ discharge constantly
- Swelling can also short the circuit.

Applications

1. Consumes electronics (mobile phones, laptops)
2. Electric vehicles

RESERVE BATTERIES

- used back in WWII (not modern)
- made for missiles and torpedoes
- mid-air crisis, nuclear weapons
- should give very high power, quick activation.
- Zn-air battery same concept; not much power.
- Almost unlimited shelf life. (primary battery)

- Batteries that are inactive when not in use and made ready for use by activating them prior to application
- Usually, one of the components is kept isolated and on demand, is released and allowed to come in contact with the other components.
- High power required for a short time (~300kW for 10 minutes)

Features

1. No self-discharge
2. Unlimited shelf life ~10 years. - components are separated
3. Quick activation - fast reaction
4. High power delivery
5. High reliability.

Types

1. Water activated - sea water (salts)
   - lifesaver jacket lights
   - table salt can be added for fresh water

2. Electrolyte activated - KOH
   - glass-covered KOH (ampule)
   - break glass and reaction occurs.

3. Gas activated
   - Cl_2, O_2 etc.

4. Thermal batteries
   - solid electrolyte becomes molten
   - starts conducting
   - for mixtures, eutectic mixture used (low MP)
   - mechanical shock

Mg-$AgCl$ Battery - water activated.

Anode : Mg - cannot be cathode
Cathode: $AgCl$.

Construction

(i) Anode

- sheet of Mg - conducting

(ii) Cathode

- sheet of $AgCl$ cannot be used alone
- not conducting
- sheet of $AgCl$, made conducting by reducing surface to Ag (photographic solution)

(iii) Electrolyte

- sea water

(iv) Separator

- needs conduction to occur fast
- cannot be SPM
- non-conductive spacer placed between the electrodes, usually in the form of discs, rods, glass beads.

Working

Anode:

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

Cathode:

$$AgCl + e^- \longrightarrow Ag + Cl^-$$

Cell reaction:

$$Mg + 2AgCl \longrightarrow Mg^{2+} + 2Ag + 2Cl^-$$

$$Mg + 2AgCl \longrightarrow MgCl_2 + 2Ag$$

Applications

1. Aviation and marine life jacket lights
2. Marine markers
3. Sonobuoys - picks up underwater movements
4. Electric torpedoes
5. Weather balloons

Advantages

1. Reliable
2. Safe
3. Instantaneous activation
4. Long shelf life
5. Lightweight (no need to carry electrolyte)
6. High discharge after activation

Disadvantages

1. Once activated, must be replaced.

FUEL CELLS

- Alternate for gasoline; hydrogen
- Redox reaction of combustion of fuels

Thermal Power Plant: the following process

chemical energy → thermal energy → mechanical energy → electrical energy

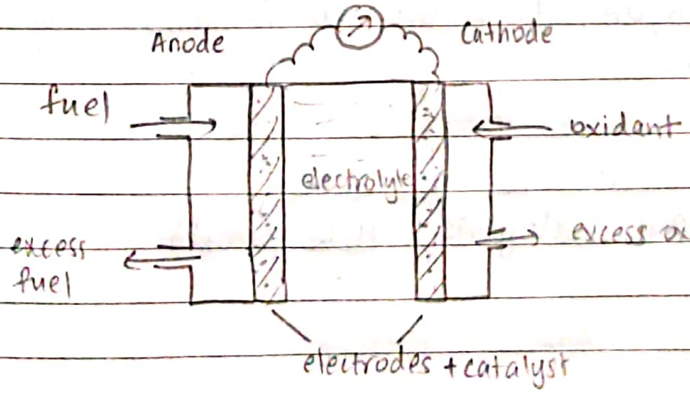
35-40% efficiency

If possible to,

chemical energy → electrical energy

75-80% efficiency

- Fuel cells can be defined as galvanic cells in which chemical energy of a fuel is directly converted into electrical energy by means of redox reactions using fuels and oxidants.
- Conceptualised in 1839 by Sir William Grove.
- Problems: transportation, mobile applications.
- NASA involved in fuel-cell technology
- Apollo used first fuel cell.



- Oxygen reduction requires catalyst (like Zn-air, page 120)

- Current α rate of reaction
- Electrode not just current collector; also site of reaction
- Electrode needs to be porous for gas to diffuse and come in contact with electrolyte.

- No electroactive material stored in fuel cell, unlike in batteries.
- Electrochemical energy needs to be supplied constan
- Battery - energy storage device
  Fuel cell - energy conversion device
- Unlimited capacity /not applied here

Cell representation

Fuel | catalyst | electrolyte | catalyst | oxidant

Working (in general)

Anode: Fuel $\longrightarrow$ oxidised product + e^-

Cathode: Oxidant + e^- $\longrightarrow$ reduced product

Fuels that can be used

- H_2, CH_3OH, CH_3CH_2OH, CO (Ellingham diagram), NH_2-NH_2, HCHO

Oxidants that can be used

- O_2, air, halogens, H_2O_2 (mild)

Advantages of Fuel cells.

1. High efficiency
2. Silent operation (compared to TPP)
3. Eco-friendly (no harmful waste products)

Disadvantages of Fuel cells.

1. Storage & transportation of H_2 and O_2
   - cryogenic, under pressure, in honeycomb structure of organic compounds (~~metal~~ frameworks), metal hydride structures under pressure, ammonia boranes - pellets. (pellets recharged with H_2)
   - Fuels need to be stored in cans under pressure and special equipment is required
2. Cost of power is very high
   - Catalysts (Pt, Rh, Pd are expensive)

TYPES OF FUEL CELLS (H_2-O_2) - based on electrolyte.

(1) Alkaline fuel cell

(i) Electrolyte is KOH
(ii) Classified as low-temperature fuel cell (~100°c)
(iii) O_2 reduction is faster in alkaline medium as compared to acid medium.
(iv) Non-noble metals can be used as catalyst (less expensive)

advantage

(v) C-containing fuels cannot be used as CO_2 is produced

$$KOH + CO_2 \longrightarrow K_2CO_3$$ - blocks sites, brings down efficiency.

(vi) Have to use very pure H_2 and O_2

Construction

(i) Anode active material : H_2

(ii) Cathode active material : O_2

(iii) Anode :

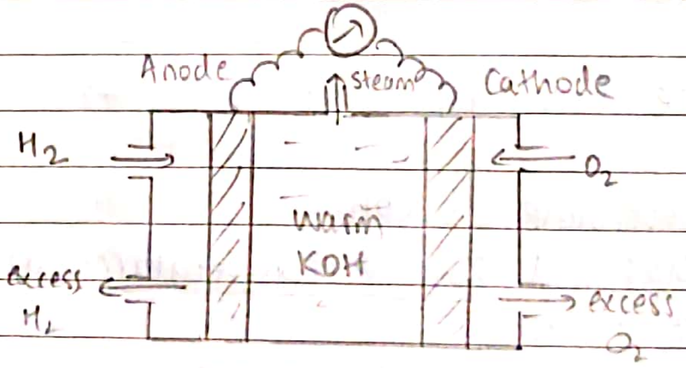
porous carbon electrode impregnated with Pt

(iv) Cathode

porous carbon electrode impregnated with Ag

(v) Electrode : 30 - 45 % KOH

Diagram



Working

Anode: $H_2 \longrightarrow 2H^+ + 2e^-$

$2H^+ + 2OH^- \longrightarrow 2H_2O$

$2OH^- + H_2 \longrightarrow 2H_2O + 2e^-$

Cathode: $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

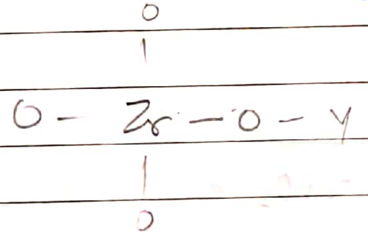
$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O.$

- emf generated : 1.23 V
- cell at 100°C as H_2O produced should not dilute the electrolyte. (KOH)
- H_2O produced in space — drank by astronauts (distilled water)
- Distilled water — good solvent — dissolves minerals from body — not that great to consume
- RO water devoid of minerals
- Some RO water is with "added minerals".

(2) Solid-oxide fuel cell (SOFC) (H_2 - O_2).

(i) Electrolyte is solid oxide (ZrO_2 doped with Y_2O_3 — creates $O_{\cancel{2}}^{2-}$ ion vacancy in lattice)

allows movement of O^{2-} ions
↓
classified as electrolyte



(ii) Cathode - O_2 undergoes reduction - jumps through electrolyte - goes to anode

(iv) Anode - H_2 - O^{2-} from lattice reacts with oxidised H_2 (H^+) to form H_2O

(v) High temperature fuel cell (~650° - 1000°C) ceramic oxides conducting only at high temperatures, only with doping

(vi) Need not use catalyst as high temperature is sufficient to facilitate reaction at a good speed. (cost is low)

(vii) CO can be used as fuel (unlike alkaline fuel cell) ⇒ very pure H_2 not required

(viii) Slow start-up (raising temperature)

- According to Nernst eq., voltage should decrease with increase in temperature.
- But, reaction more efficient at high-temp.

(ix) Due to high temperature, corrosion of equipment is more.

Construction

(i) Anode active material : H_2

(ii) Cathode active material: O_2

(iii) Anode:

$Co-ZrO_2$ or $Ni-ZrO_2$

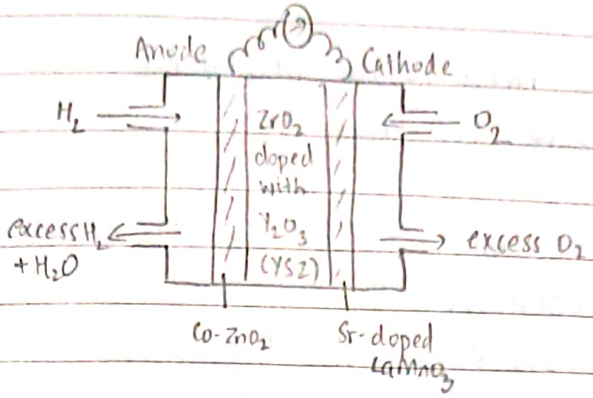
(iv) Cathode:

Sr-doped $LaMnO_3$ (Lanthanum manganite)

(v) Electrolyte

ZrO_2 doped with Y_2O_3 (YSZ- Yttria Stabilised Zirconia)

Diagram



Working emf = 1.23 V

Cathode : $\frac{1}{2} O_2 + 2e^- \longrightarrow O^{2-}$

Anode : $O^{2-} + H_2 \longrightarrow H_2O + 2e^-$

Cell reaction: $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$

- water formed at anode

(3) Polymer - electrolyte membrane fuel cell] PEMFC
Proton - exchange membrane fuel cell

(i) Electrolyte is polymer ((solid) eg: SO_3H^- added to teflon) capable of exchanging H^+
fluorocarbon polymer backbone
called NAFION - DuPont company

(ii) Low temperature fuel cell (~80°C)

(iii) O_2 has to reduce in acidic medium; we have to use Pt as a catalyst as reduction is slow and is at low temperature
Noble metals like Pt have to be used.

(iv) Energy density very high; thickness of polymer ~50 μm (unlike OH and solid-oxide); very light and low volume

(v) CO should be absent — acts as catalytic poison for Pt
- H^+ ions need to be produced
- Very pure H_2 and O_2

(vi) Expensive cell
- Pt expensive
- NAFION expensive (polymer)
- Pure H_2 and O_2 need to be use

Construction

(i) Anode active material: H_2

(ii) Cathode active material :- O_2

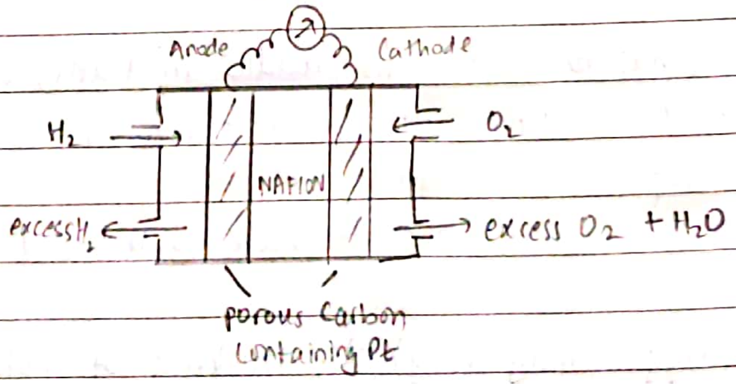
(iii) Anode: Porous carbon containing Pt

(iv) Cathode: Porous carbon containing Pt.

(v) Electrolyte:

fluorocarbon polymer backbone with SO_3H groups

Diagram



Working

Anode: $H_2 \longrightarrow 2H^+ + 2e^-$

Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O$ — reduction of O_2 in acidic medium

Cell reaction: $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$

emf = 1.23 V

- water formed at cathode.

Water management of cell

- too high temp → polymer dehydrated → polymer cracked → short circuit
- polymer needs to be wet to conduct H^+ ions
- has to be less than 100°c

- too low temp → reaction will be slower → large amount of catalyst
- too much H_2O → cell flooded → diffusion of reactants slow and difficult.

APPLICATIONS OF FUEL CELLS.

- Vehicle traction for cars, buses and electric vehicles.
- Space exploration
- Large-scale power generation.

Efficiency of Fuel Cell

$$\eta = \frac{\overset{\text{electrical work}}{\Delta G}}{\underset{\text{combustion}}{\Delta H}} \times 100\% = \frac{-nEF}{\Delta H} \times 100\%$$

Q1: Find η of H_2-O_2 alkaline fuel cell and compute E°_{cell}.

$\Delta_f H^\circ_{(H_2O)} = -285.8\ kJ\ mol^{-1}$, $\Delta G^\circ = -237.2\ kJ\ mol^{-1}$

standard is for std. conditions (liquid H_2O)

for 1 mol H_2 undergoing combustion

$\eta = \frac{\Delta G^\circ}{\Delta H} = \frac{-237.2}{-285.8} = 0.8299 = 83\%$

anode: $H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$

cathode: $H_2O + \frac{1}{2}O_2 + 2e^- \longrightarrow 2OH^-$

$$\Delta G^\circ = -nE^\circ F$$
$$+237.2 \times 10^3 = +2 \times E^\circ_{cell} \times 965\cancel{00}$$
$$\frac{2372}{2 \times 965} = E^\circ_{cell} = 1.229\ V$$
$$\boxed{E^\circ_{cell} = 1.23\ V}$$

Q2: Calculate efficiency of $CH_3OH - O_2$ fuel cell. $E^\circ_{cell} = 1.2V$

$\Delta H_{(combustion)} = -726\ kJ\ mol^{-1}$

cell reaction: $CH_3OH + 2O_2 \longrightarrow CO_2 + 2H_2O$

anode: $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

cathode: $\frac{3}{2}O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O$

$$\eta = \frac{-nEF}{\Delta H} = \frac{-6 \times 1.2 \times 965\cancel{00}}{-726 \times 10^3} = 95.7\%$$

- acid electrolytes (H_2SO_4) will be very useful; polymer (NAFION)

O_2 SENSOR

- Device that measures the proportion of O_2 in the gas or liquid being analysed.
- First made by Bosch in 1960s.
- Divers – O_2 cylinders require sensors.
- Right proportion of O_2 required; pure O_2 is harmful (used as anaesthesia)
- Divers use if

1. Divers use it to measure partial pressure of O_2.
2. Scientists use it as probes to measure respiration and production of O_2
3. Oxygen analysers in medical applications such as respirators, anaesthetic monitors
4. Measure exhaust gas concentration of O_2 in IC engines

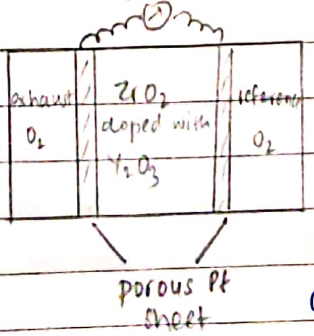
Use of O_2 Sensor (λ sensor) in Automobiles

- Correct ratio for complete combustion is 14.7:1 air:fuel
- Not always maintained
- O_2 sensor placed near exhaust and measures O_2 → sends information to engine control unit → changes ratio.
- rich mixture (too much fuel) → O_2 in exhaust less → 0.8 V
  lean mixture (little fuel) → O_2 in exhaust more → 0.2 V
  ideal mixture → 0.45 V

Diagram

(300ms) ~~times a minute~~

exhaust is at / high temp (~360°c)



(electrode type concentration cell)

cathode: $O_2 + 4e^- \longrightarrow 2O^{2-}$

anode: $2O^{2-} \longrightarrow 4e^- + O_2$

Nernst equation: $E = \frac{2.303RT}{4F} \log \frac{p_{o}^{\text{ref. } O_2}}{P_{\text{exhaust } O_2}}$

- Only unleaded gasoline can be used.
- Petrol — anti knock - avoid damage
- Tetra-ethyl lead used to be anti-knock
- Unleaded gasoline uses methyl-tert-butyl ether

- Pb will poison the Pt

Rich mixture

CO, C, unused fuel are pollutants

Lean mixture

NO_x gases pollutants (cause acid rain)

- NO_x need to undergo reduction to become benign

λ sensor

- λ is the ratio of amount of O_2 actually present in the combustion chamber compared to the amount that should be present to obtain complete combustion.
- Lean mixture: $\lambda > 1$.
  Rich mixture: $\lambda < 1$

Symptoms of failure of O_2 sensor

- Increased tailpipe emissions
- Increased fuel consumption
- Hesitation on acceleration

discharge, charge very fast

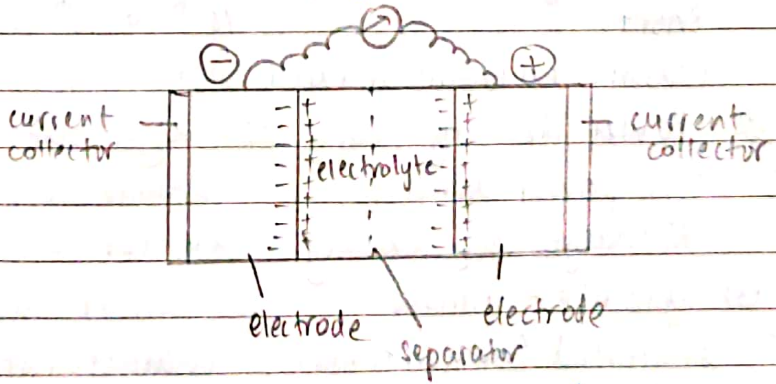
SUPERCAPACITOR

- Supercapacitors are devices that have very high capacitance and are used to store extremely large amounts of electrical charge.
- They are also known as electrochemical double layer capacitors (EDLC) or ultracapacitor
- They charge and discharge very quickly as compared to batteries.
- Their capacitance can be as high as 1000s of Farads.

Construction

- Two electrodes in contact with an electrolyte.
- An ion-permeable separator is placed between the electrodes (to prevent electrical contact)
- The separator is sandwiched between the electrode
- This is placed in a housing.
- The electrolyte is poured inside and sealed.
- The electrodes are flanked with the current collectors.

Diagram



Working

- When the supercapacitor is charged (a potential is applied on the positive electrode), negative ions get attracted to the positive electrode, giving rise to an electric double layer with a charge separation in the nanometer range.

- Similarly, -ve electrode attracts +ve ions from electrolyte, forming an electric double layer

(1) Capacitance ∝ surface area ($C = \frac{\varepsilon A}{d}$)
∴ electrodes are porous.

(2) The +ve and -ve charges are not due to any chemical reactions

Materials for electrodes

- activated carbon, graphene, carbon nanotubes, some conducting polymers

Materials for electrolytes

KOH, H_2SO_4, organic solutions of Li salts

Materials for separator

porous polypropylene

Characteristics

Advantages	Disadvantages
(1) Charging time - very short reason: no chemical rxn	(1) Energy density - very low; 1/5th to 1/10th of a battery; ∴ cannot replace batteries
(2) Power density - very high power density; discharge very quickly	(2) High self discharge - loses charge very quickly (cannot use for SLI)
(3) Cycle life - almost unlimited (million times)	(3) Linear discharge voltage characteristics (V-t graph)
(4) Safety - more tolerant to abuse; very safe	(4) High cost
	(5) Power is available for a short duration

camera flash uses capacitor (charges ↓ discharges)

no rxns, phase changes

Applications

1. Flash photography in digital cameras
2. Emergency kits
3. Memory backup (fluctuating voltage)
4. Drilling machines in space
5. Hybrid cars - start & stop applications (regenerated braking)

Differences between Battery and Supercapacitor

Property	Battery	Supercapacitor
(1) Charging time	long	very short
(2) Principle of working	chemical rxn releases energy (redox reaction)	ions get attracted to opposite terminal and form double layers
(3) Power density	moderate to low (depends on species)	very high
(4) Function	gives emf to load (source of energy)	stores electrical energy
(5) Discharge voltage	linear v-t graph	roughly constant until cutoff
(6) Energy density	moderate to high	very low
(7) Cycle life	depends on battery construction	almost unlimited
(8) Self-discharge	low to moderate	very high

RAGONE PLOT

- Energy density vs power density of all devices