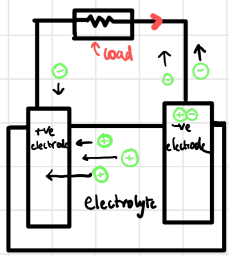
Energy Storage Devices, Hydrogen Storage, and Sensors

Battery

Device which stores chemical energy & converts to electrical energy
↳ Used in :
Mobiles, Laptops, Calculators

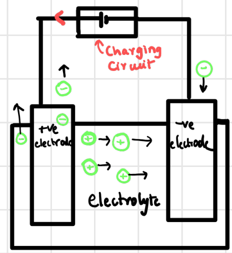
- **Discharging,**
  Delivers Power
  Galvanic Cell

  A: $M \rightarrow M^{n+} + ne^-$
  C: $A + ne^- \rightarrow A^{n-}$
  $M + A \rightarrow MA$



- **Charging**
  Consumes Power
  Electrolytic Cell

  Anode : $A^{n-} \rightleftharpoons A + ne^-$
  Cathode : $M^{n+} + ne^- \rightleftharpoons M$
  Overall : $MA \longrightarrow M + A$



Components of a Battery

- **Anode** : Oxidation
  Electroactive material : Zn, Pb, Li
- **Cathode** : Reduction
  Electroactive material : PbO_2, MnO_2, O_2
- **Electrolyte** : Good Ionic Conductivity
  Acid, Alkali/Salt Solⁿs , Solids doped oxides , polymers, H_2SO_4, KOH, Nafion etc.,
- **Seperator** : Insulator which seperates anode & cathode
  Prevents Internal Short circuit
  Transports ions from anode to cathode
  Polypropylene, Cellophane

Types of Batteries

PRIMARY

- One time use
- Irreversible batteries

ex: Dry Cell (Leclanche cell), $LiMnO_2$

SECONDARY

- Reverse r/n possible by supply of current
- Regenerates electroactive species
- Reversible / Storage batteries

ex: Pb-acid battery , Li-ion, Ni-Cd
↳ Phone Battery (Li-ion)
↳ Hazardous to water bodies (Ni-Cd)

BATTERY Characteristics

VOLTAGE

$$E_{cell} = E^{o}_{cell} - \frac{2.303RT}{nF} \log Q$$

Factors affecting Voltage :

- higher E^{o}_{cell} / $E^{o}_{cathode} - E^{o}_{anode}$ ⇒ higher E_{cell}
- Temp ↑ ⇒ E_{cell} ↓
- Q ↑ ⇒ E_{cell} changes marginally

CURRENT (A, mA)

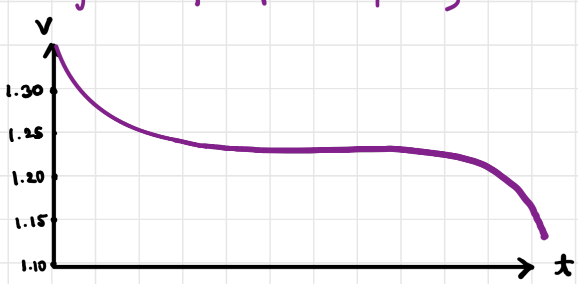
- Measure of rate at which battery discharges
- Depends on rapid electron transfer r/n
  - E_{cell} close to E^{o}_{cell} if small concentration
  - Highly conducting electrolyte offers resistance & I_{max} is less
  - Reduce interelectrode distance ($R \propto l$)

CAPACITY (Ah)

- Charge / Amount of electricity obtained from battery
- $C = \frac{wnF}{M}$

C : Capacity
w : mass   n : no of e^-
M : Molar mass of active material
F : 96500 C mol^{-1} (Faraday's Constant)

- Capacity depends on:
  - Size of battery
  - Discharge conditions of battery
- $C = It$
- Longer the flat portion of curve, Better the Capacity



ELECTRICITY STORAGE DENSITY

- Amount of Charge per unit weight which battery can hold
- Weight includes :
  - Electrodes
  - Electrolytes
  - Case
  - Current Collectors
  - Terminals etc.,

$$ESD = \frac{\text{Capacity}}{\text{Wt. of battery}}$$

ex: 7g of Li gives 1F of charge
104g of Pb also gives 1F of charge

CYCLE LIFE

- No. of charges/discharges possible before any failure
- Only for rechargable batteries
- Reasons for limited cycle life :
  - Corrosion at contact points
  - Shedding of active material from plates
  - Shorting between electrodes due to irregular crystal growth & changes in morphology

ENERGY EFFICIENCY

- $\%$ of E.E $= \dfrac{\text{Energy released on discharging}}{\text{Energy required for charging}} \times 100$
- Depends on efficiency of electrode r/ns

SHELF LIFE

- Max time for which battery can be stored w/o loss of performance
- Lower shelf life due to self discharge

TOLERANCE TO SERVE CONDITIONS

- Battery must be able to tolerate conditions like :
  - Temperature
  - Vibration
  - Shock etc.,

ENERGY DENSITY (wt-hr/kg)

- $E.D = \dfrac{\text{Energy available from battery}}{\text{Mass of the battery}}$

- $E.D = \dfrac{i \times E_{cell} \times t}{W}$

W : mass of battery
i : current
t : time

POWER DENSITY (wt/kg)

- $PD = \dfrac{\text{Power available from battery}}{\text{Mass of battery}}$

- $PD = \dfrac{i \times E_{cell}}{W}$

$= \dfrac{ED}{t}$

Q. 1. A battery using Zn as anodic material lasts for 2 hours when a constant current of 1.25 A is drawn from it. What weight of Zn is present in the battery if the reaction at the anode is

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

If the electricity storage density of the battery is 180 As/g, determine the weight of the entire battery.
(Given : molar mass of Zn = 65 g, F = 96500 C/mol)

A. $t = 2 \times 60 \times 60\ s$; $M_{Zn} = 65g$; $I = 1.25A$;

$ESD = \dfrac{C}{\text{Wt of battery}} = 180\ As/g$

$C = It$

$= 1.25 \times 2 \times 60 \times 60$

$= 9000\ As$

$\text{Wt of battery} = \dfrac{\cancel{9000}^{50}}{\cancel{180}}$

$= 50g$

Q 2. Calculate the electricity storage density of a Lithium battery which has 2.0 g of lithium as anodic material. The total weight of the battery is 65 g. Give the answer in Ah/kg.
(Given : Atomic mass of lithium is 7)

A. $C = \dfrac{WnF}{M} = \dfrac{2 \times 1 \times 96500}{7} = 27571.42\ As$

$= 7.658\ Ah$

★ $\boxed{1\ Ah = 3600\ A\text{-}s}$

$ESD = \dfrac{C}{\text{Wt of battery}} = \dfrac{7.658}{65 \times 10^{-3}} = 117.81\ Ah/kg$

3. Calculate the energy density and power density of 20 kg Lead acid battery which contains 5 kg lead as anode material and discharges constant current for 10 hours. The voltage of the battery is 2 V.
(Given : Atomic mass of lead is 207.2, number of electrons transferred in the redox reaction is 2, F= 96500 C/mol)

A. $C = \dfrac{WnF}{M} = \dfrac{5 \times 10^3 \times 2 \times 96500}{207.2}$

$= 4657335.9\ As$

$= 1293.7\ Ah$

$ED = \dfrac{V \times It}{W} = \dfrac{\cancel{2} \times 1293.7}{\cancel{20}\ 10} = 129.37\ wh/kg$

$PD = \dfrac{ED}{t} = \dfrac{129.4}{10} = 12.94\ W/kg$

4. Calculate the efficiency of H_2-O_2 alkaline fuel cell .
[Given: E^o_{Cell} =1.20 V, $\Delta H_{f(H2O)}$ = -285.8 kJ/mole]

A. $\eta = \dfrac{\Delta G}{\Delta H} \times 100 = \dfrac{-nFE}{\Delta H} \times 100 = \dfrac{-2 \times 965\cancel{00} \times 1.2}{-285.8 \times 10\cancel{00}}$

$= 81\%$

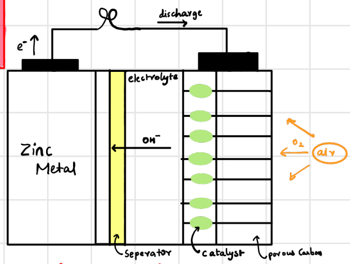
5. If E^o_{Cell} for H_2-O_2 alkaline fuel cell is 1.23 V and efficiency is 83%, calculate the heat evolved during the reaction.

A. $\eta = \dfrac{\Delta G}{\Delta H} \times 100$

$83 = \dfrac{-nFE}{\Delta H} \times 100 = \dfrac{-2 \times 96500 \times 1.23}{\Delta H} \times 100$

$\Delta H = \dfrac{-2 \times 96500 \times 1.23 \times 100}{83} = -286\ kJ$

MODERN BATTERIES



Anode:

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

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

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

Cathode:

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

Overall:

$Zn + \frac{1}{2}O_2 \rightarrow ZnO$

Emf = 1.2V

- **Zinc-air Battery**
  - Alkaline Battery
    Electrolyte : alkali
  - Uses oxygen directly from atmosphere to produce chemical energy
  - Cathode active material need not be stored inside battery
  - High Energy density

- Construction :

  Anode :
  - Zn granules & small amount of electrolyte

  Cathode :
  - C (Graphite) blended with MnO_2 (catalyst) with wet proofing agent coated on Ni wire mesh support & outer layer of air permeable Teflon layer.
  - Air access holes on cathode provide pathway for O_2 to enter battery

  Electrolyte :
  - 30% KOH

  Seperator :
  - Polypropylene member soaked in electrolyte

- Advantages :
  - High ESD because air comes from atmosphere & not added to battery mass
  - Very long shelf life
  - No ecological problems & Inexpensive
- Disadvantages :
  - Low output power
  - Efficiency is low because CO_2 also may enter and
    $CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O$
- Applications :
  - Power source in hearing aids & medical devices
  - Voice transmitters
  - Rail-road signalling

- **Lithium Batteries**
  - Li is popular anodic material because:
    - Light weight metal.
    - High electrochemical equivalence (7g of Li ⇒ 1F of charge)
    - High negative standard reduction potential (−3.05 V)
    - Gives high voltage when coupled with other electrodes
  - Aq. electrodes can't be used because Li is very reactive & reacts vigorously with water
  - Instead organic & inorganic electrolytes are used.

  - Li battery consists:
    - Li as anode
    - MnO_2, SO_2Cl_2 as cathode
    - Electrolyte can be $\underbrace{\text{acetonitrile, propylene carbonate}}_{\text{Organic Solvents}}$, $\underbrace{SOCl_2}_{\text{Inorganic Solvents}}$

    - Primary Li batteries : Li − MnO_2
      Secondary Li batteries : Li-ion battery

  - Advantages:
    - High Voltage upto 4V
    - High Energy density
    - High tolerance
    - High ESD
    - Flat discharge characteristics

  - Disadvantages:
    - Safety concerns due to high reactivity
    - Poor cycle life (dendrite formation)
    - Transportation limit

Lithium Ion Battery

- **Principle :**
  - Li ion moves from Anode $\longrightarrow$ Cathode $\Rightarrow$ Discharging
    and Anode $\longleftarrow$ Cathode $\Rightarrow$ Charging
  - Materials used as anode & cathode are capable of lodging Li ions
- **Construction :**
  - Anode : Lithiated Carbon (Graphite) coated on Cu current collector
  - Cathode : Lithiated transition metal oxide coated on Aluminium Current Collector ($LiCoO_2$)
  - Electrolyte : Mixture of organic carbonate solvents like ethylene Carbonate (or) diethyl carbonate containing Lithium salts like $LiPF_6$, $LiClO_4$
  - Seperator : Very thin sheet of micro perforated polypropylene membrane
- **Working :**
  - Charging

  - Discharging

- **Reactions:**

Charging:

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

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

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

Discharging:

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

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

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

- **Advantages :**
  - Lighter than rechargable batteries
  - Li-ion battery delivers high voltage (3.7V)
  - Low self-discharge rate
  - Don't suffer battery memory effect
  - Good cycle life as problem of dendrite formation is eliminated

Latest Materials in use

- $LiNiCoAlO_2$
- $LiNiMnCoO_2$ → Tesla, Panasonic
- Li_2TiO_3 → As anode & $LiMnO_2$ as Cathode

- **Disadvantages :**
  - Rising internal resistance with cycling & age
  - Safety concerns if overheated / overcharged

RESERVE BATTERIES

- Batteries inactive when not in use and made ready by activation prior to use.
- Key component is usually isolated & brought to contact only when required (Usually Electrolyte)
- Self discharge is prevented
- Unlimited Shelf life
- For emergency crises

- <u>Salient Features</u>:
  - Quick activation
  - High Power for short time
  - No self discharge
  - Unlimited Shelf life (10 yrs)
  - High reliability

  ex: Mg – AgCl (water activated)
  Zn – Ag_2O (KOH activated)

TYPES OF RESERVE BATTERIES

- **Water-activated batteries**
  - Activation by fresh or sea water
- **Electrolyte-activated batteries**
  - Activation by the electrolyte
- **Gas-activated batteries**
  - Activation by introducing a gas into cell
- **Heat-activated / Thermal batteries**
  - A solid salt electrolyte is heated to molten condition
    It becomes ionically conductive, thus activating cell

- ## Mg-AgCl battery water activated battery

- **Construction**:
  - Anode: Mg sheet
  - Cathode: AgCl sheet (non conductive)
    ↳ made conductive by reducing surface to Ag
  - Seperators: Non-conductive spacers in form of discs, rods, glass beads (or) absorbent fabric
  - Electrolyte: Sea water
- **Working**:
  - Anode: $Mg \longrightarrow Mg^{2+} + 2e^-$
  - Cathode: $2AgCl + 2e^- \longrightarrow 2Ag + 2Cl^-$

  Overall: $Mg + 2AgCl \longrightarrow 2Ag + Mg^{2+} + 2Cl^-$
- **Advantages**
  - Safe & Reliable
  - Instant activation
  - Long Shelf life
  - Less weight
- **Disadvantages**
  - High discharge after activation
  - Must be replaced after activated
- **Applications**:
  - Sonobuoys
  - Weather balloons
  - Pyrotechnic devices
  - Emergency lights
  - Electric torpedos
  - Air-sea equipment
  - Marine markers

~~Fuel Cells~~ FUEL CELL

- Chemical Energy $\xrightarrow[\text{Cells}]{\text{Fuel}}$ Electrical Energy through redox r/n
- It is a Galvanic Cell
- Don't store energy. Converts chemical to electrical energy
- Fuel & Oxidising agents must be continuously supplied at electrodes

- **Construction**
  - 2 Electrodes
  - Catalyst
  - Electrolyte
  - Electroactive material
- **Working**
  - Anode : Fuel $\rightarrow$ Oxidation product + ne^-
  - Cathode : Oxidant + ne^- $\rightarrow$ Reduction Product
  - Fuels : H_2, CO, CH_3OH, C_2H_5OH, $HCHO$, N_2H_4
  - Oxidants : O_2, H_2O_2, Halogens.
- **Advantages**
  - High Power efficiency (50-80%)
  - Ecofriendly
  - Silent Operation
- **Disadvantages**
  - Very expensive
  - Power Output is moderate
  - Special equipment required
- **Applications**
  - Space Exploration (Auxiliary Power Generators)
  - Vehicle traction for cars, buses etc.,
  - Large Scale Power Generation

- **Efficiency of Fuel Cell**
  - $\eta\% = \frac{\Delta G}{\Delta} \times 100 = \frac{-nFE}{\Delta H} \times 100$

TYPES OF FUEL CELLS (BASED ON ELECTROLYTE)

Alkaline Fuel Cell

- Electrolyte is aq. KOH
  Low temp fuel cell
  Faster Oxygen reduction than acid electrolytes
- Use of Non-noble metal catalyst is feasible
- Carbon containing fuels can't be used ($CO_2 + KOH \longrightarrow K_2CO_3 + H_2O$)

Phosphoric Acid Fuel Cel

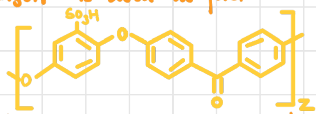
- Conc. H_3PO_4 is used as electrolyte
- Oper around 160°–220°C
- Pt is used as electrocatalyst
- only H_2 used as fuel
- H_2 must be very pure (Sulphur compounds & CO poisons the catalyst)

Molten Carbonate Fuel Cell

- Molten Carbonates ($LiAlO_2 + K_2CO_3 + Li_2CO_3$) used as electrolyte
- Operates around 600°–650°C
  No Catalyst required (High Temp)
- H_2 (or) CO used as fuel

• Polymer Electrolyte Membrane Fuel Cell

- Also called proton exchange membrane fuel cell.
- Polymer membrane is used as electrolyte
- Sulphonic acid group ($-SO_3H$) is attached to Fluoro Carbon back bone ($-CF_2-CF_2-$)
- Aquivion $-(CF_2-CF_2)_n-(CF_2-CF_2)_m-$ with side chain $OCF_2CF_2SO_3H$
- Nafion $-(CF_2-CF_2)_n-(CF_2-CF_2)_m-$ with side chain $OCF_2CFCF_3-OCF_2CF_2SO_3H$
- New membranes are being used especially when CH_3OH is used as fuel
  SPEEK (Sulphonated poly ether ether Ketone)



- Operates around 60°-90° C
- Polymer membrane MUST be hydrated to maintain H^+ conductivity
- Cathode shouldn't have any water
  - High Temp ⇒ Dehydrate Polymer (leading to crack polymer & short circuit)
  - Low Temp ⇒ Flooding of cell (Reduces efficiency & higher cata loading req)
- Low Weight
  Low Volume
  High Energy Density
  Noble Metal Catalyst (Pt)
- CO (If present) poisons the catalyst

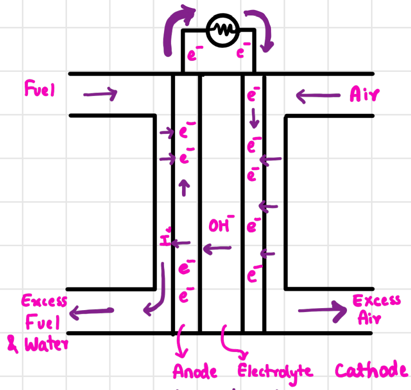
• Solid Oxide Fuel Cell

- Ceramic Oxide used as electrolyte
  ↳ ZrO_2 doped with Y_2O_3
- Operates around 650°-1000°C
- Inexpensive Catalyst
- CO used as fuel
  Slow start-up

H_2O_2 Alkaline Fuel Cell

- aq. KOH is used as electrolyte
- Low Temp fuel cell
- Oxygen reduction is more rapid in it than acid fuel cells.
- Use of non-noble metal electro-catalyst is feasible.
- Carbon containin fuel can't be used.

ex: $KOH + CO_2 \rightarrow K_2CO_3 + H_2O$ $\Rightarrow$ K_2CO_3 reduces efficiency



$H_2 | Pt | KOH | Ag | O_2$

- **Construction**
  - Anode : Porous Carbon impregnated with Pt Catalyst
  - Cathode : Porous Carbon impregnated with Ag Catalyst
  - Fuel : Hydrogen Gas
  - Oxidant : Oxygen Gas
  - Electrolyte : 30-45% KOH (warm)

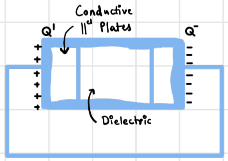
- **Working**
  - Anode : $H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$
  - Cathode : $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$
  - Overall : $H_2 + \frac{1}{2}O_2 \quad H_2O$
  - Cell operates at 100°C so that wates from KOH escapes as steam
  - This water was used by astronauts
  - Emf = 1.23V

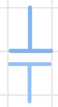
- **Advantages**
  - Operates at low temp.
  - Inexpensive because alk metal catalyst is used

- **Disadvantages**
  - Reactants must be free from C, as CO_2 formed on oxidation leading to Carbonate formation thus reducing efficiency
  - Liquid electrolytes can't be handled easily

Capacitor

- 2 Terminal electrical component that has ability to store energy (form of electrical charge)
- H 2 conducting plates seperated by a capacitor
- When DC Voltage is connected across capacitor, one plate becomes +ve & other -ve
- Charge accumulation on plates creates potential difference

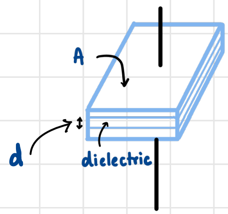




Symbol

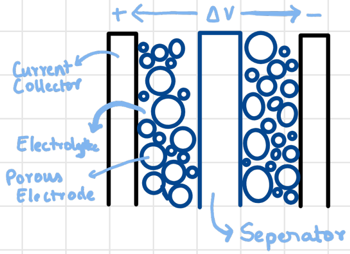
Q → Charge   V → Voltag   ⇒ $Q = CV$ → Capacitance (F / Farads)

- $C \propto \frac{A}{d}$ — A → Area of plates, d → distance b/w plates



SUPER CAPACITOR

- Also called ultra-capacitors / electrochemical double layer capacitors (EDLC)
- High Capacitance units used to store large amounts of charge
- Charge & Discharge quickly
- **Construction**
  - Electrodes : high surface area materials like porous carbon, graphene, carbon nanotubes & contain conducting polymers (or) carbon aerogel
  - Electrolyte : KOH, H_2SO_4 , Na_2SO_4
  - Seperators : Ion permeable seperator sandwiched b/w electrodes in order to prevent electrical contact but allows ions to flow thro (ex: porous polypropylene)



- **Working**
  When potential is applied, +ve electrode attracts −ve ions
  −ve electrode attracts +ve ions
  - Formation of electrical double layer at entire electrode/electrolyte interface with charge seperation (in nm)
  - Only absorption & desorption takes place. No redox r/n

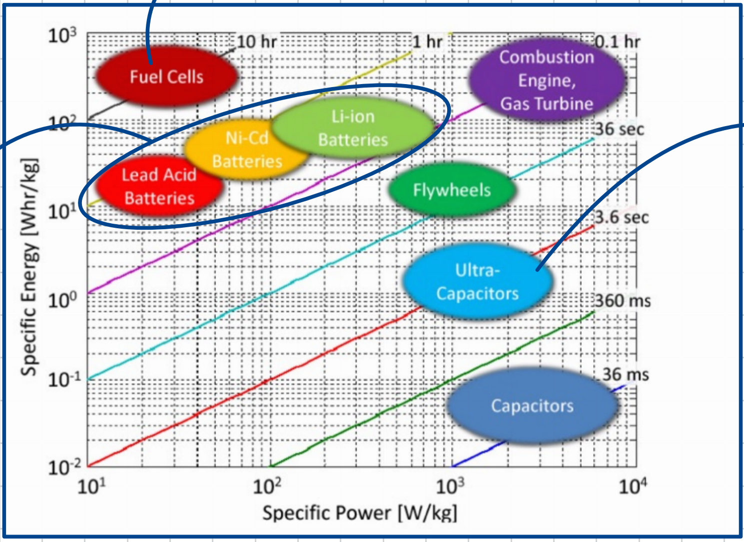
- d is very small (in nm)   A is very arge
  $C \propto A/d \Rightarrow C$ is also very large
- Formation of electrical double layer at each electrode interface,
  C_T (Total Capacitance) $\Rightarrow \frac{1}{C_T} = \frac{1}{C_+} + \frac{1}{C_-}$
  C_- → Anode Capacitance
  C_+ → Cathode Capacitance

- **Advantages**
  - Rapid Charging
  - High Power Density
  - High Cycle Life
  - Safe (Low internal Resistance & heating rates)
- **Disadvantages**
  - Low Energy Density
  - High Self Discharge
  - Linear Discharge voltage
  - High cost
  - Power available for short time
- **Applications**
  - Memory Back-up
  - Hybrid Cars for start & stop
  - Flash photography (Digital Camera, Flash light etc.,)
  - Intermediate energy storage (FM, cellphones & emergency kit)

RAGONE PLOT

- Energy Density v/s Power Density Plot
- Used to compare performance of various energy storage devices

High Energy Density
Low Power Density



Moderate
E.D & P.D

High P.D
Low E.D

E.D Increases

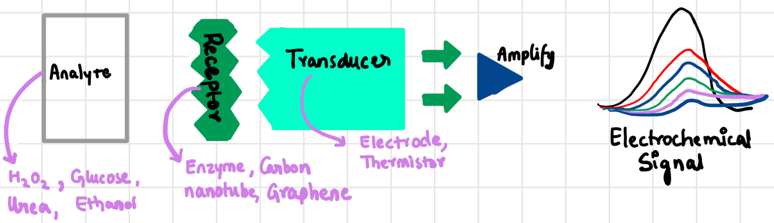
PD Increases

SENSOR

- A device that detects & responds to some type of input from environment
  - Input can include :
    - Light
    - Heat
    - Motion
    - Moisture
    - Pressure

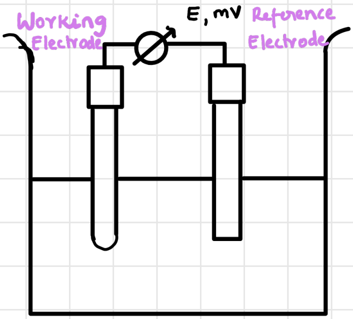
- Types of Sensors
  - Semiconductor Sensors ⇒ Galium Arsenide , Ge & Si - Solar C
  - Mass-Sensitive Sensors ⇒ Piezoelectric material - Weight Measurement
  - Conductivity Sensors ⇒ Platinum Foil - Measures Conductivity in aq sol^n
  - Capacitive Sensors ⇒ Can detect all types of metals, plastics, wood, paper, glass & cloth
  - Thermometric Sensors ⇒ Thermocouple, Thermistors & Semiconductor Based ICs
  - Calorimetric Sensors ⇒ Determines the change in enthalpy of chemical substances
  - Electrochemical Sensors ⇒ Glucose Sensor (Measures Current)
  - Optical Sensors ⇒ Medical Application in pulse oximeter

- **ELECTROCHEMICAL SENSORS**
  - An electrode is used as a transducer in presence of analyte
  - It transfers effect of electrochemical interaction of analyte into useful electric signal



- 3 Types of Electrochemical Sensors :
  - Potentiometric Sensors
  - Amperometric Sensors
  - Electrochemical Sensors

- ## POTENTIOMETRIC SENSORS
  - Sensor that use conc. on equilibrium of redox r/n at electrode-electrolyte of an electrochemical cell.



  - Oxidant $+ne^- \longrightarrow$ Reduced Product
    Takes place at electrode surface
  - Mainly determines analyte conc.

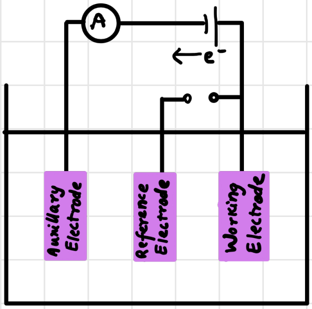
$$E_{cell} = E^0_{cell} + \frac{RT}{nF} \log\left(\frac{C_O}{C_R}\right)$$

at 298°, $E_{cell} = \frac{0.0591}{n} \log\left(\frac{C_O}{C_R}\right)$

ex:
- Ion Selective Electrode Sensors
  - Glass Electrodes
  - Solid membrane Electrodes
- Gas Potentiometric Sensors
  - pH meter based gas electrodes
  - Solid Oxide Sensors

- **Advantages :**
  - Detection of various analytes qualitatively & quantitatively
  - Easy Construction, Accurate, Sensitve, Highly selective determination
  - Small volumes of analytes can be measured
  - Economically Viable
- **Disadvantages :**
  - Calibration must be done
  - Impurities can affect Potential Values
  - Temperature also affects Potential Values

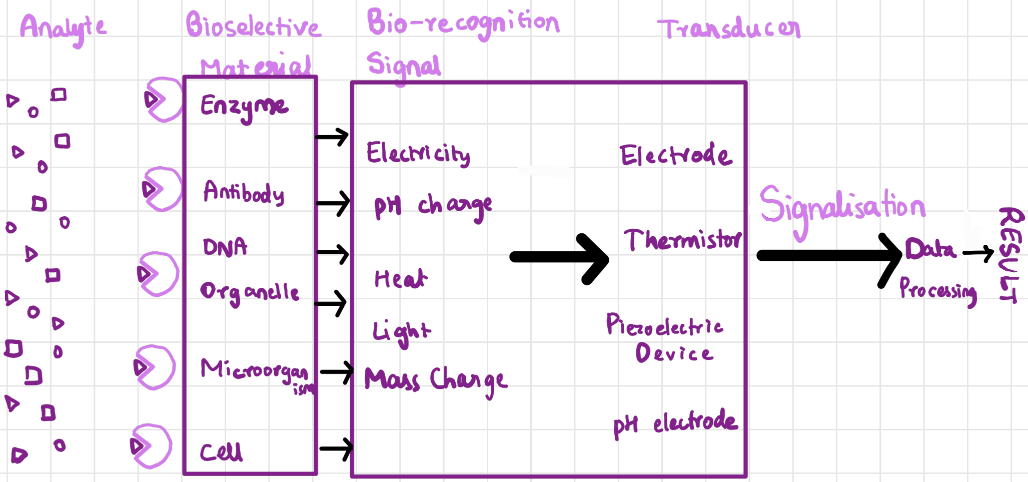
- **AMPEROMETRIC SENSORS**
  - Measure current in response to detect concentration of analyte at fixed potential
  - Applied potential drives e^- transfer r/n of analytes & measured current indicates analyte concentration
  - Amperometric sensors quantify current output b/w Working & Reference electrode. The sensor is usually composed of 3 electrodes (working, auxillary, reference)



- <u>Working</u>
  - The reference electrode ($Ag|AgCl$, $Hg|Hg_2Cl_2$) provides a stable potential compared to working electrode.
  - An inert conducting material (Pt, Graphite) is used as auxillary electrode
  - Supporting electrolyte is used in controlled - potential experiments to eliminate electromigration effects, decrease resistance of sol^n & maintain ionic strength constant
- <u>Advantages</u>
  - Used for estimation of reducible & non-reducible analytes (Mg^{2+}, PO_4^{3-}, SO_4^{2-})
  - More Sensitive & Accurate
  - Traces of reducible species can be determined accurately
  - Simple Operation & Easy construction
- <u>Disadvantages</u>
  - Working potential can be applied only for limited time
  - Coprecipitation gives inaccurate results
  - Sensors can't use voltage less than −2V else, Hydrogen is evolved
  - Consumes more time to remove dissolved Oxygen

- **ELECTROCHEMICAL BIOSENSORS**
  - An analytical device used to determine presence & concentration of specific substance in biological analyte

Input → BIOSENSOR → Output

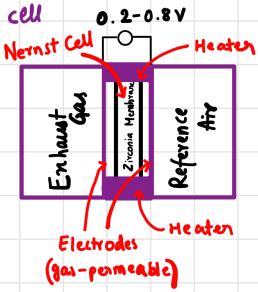


- <u>Advantages</u>
  - Easy to miniaturize & excellent detection limits
  - Ability to be used in turbid biofluids with optically absorbing & fluorescing compounds
  - Infectious diseases can be easily detected

- <u>Disadvantages</u>
  - Can't be used in high temp.
  - Poor Sensitivity
  - Low Shelf life

OXYGEN SENSORS

- A device that measures proportion of O_2 in gas/liquid being analysed
- **Applications**
  - Divers use to measure partial pressure of O_2 in their breathing gas
  - Scientists use as probes to measure respiration / production of O_2
  - O_2 analyzers used in medical application like anesthesia monitors, respirators etc
  - Measure exhaust gas concentration of O_2 in IC engines
- **Principle** (Role in automobiles)
  - Stoichiometric air/fuel ideal ratio for combustion is 14.7 : 1
  - Located in exhaust stream & indirectly determine air/fuel ratio
  - O_2 sensor allows engine control system to maintain ideal ratio across various engine operating systems.
  - Compares amount of O_2 in exhaust to atmosphere
  - Output Voltage is based on difference in O_2 conc. in exhaust & atmosphere
  - Output of 0.2V → Lean Mixture
    0.8V → Rich Mixture
    0.45V → Ideal Set Point
  - Voltage is sent as feedback to ECU which adjusts $\frac{\text{air}}{\text{fuel}}$ ratio back to stoichiometric value
  - Lean mixture results to NO_x emissions
    Rich mixture leads to CO, C particles & unburnt fuel emissions
  - Based on solid state electrochemical fuel cell
  - Operates at 360°C minimum



- **Construction**
  - Anode : Pt
  - Cathode : Pt
  - Electrolyte : ZrO_2 doped with Y_2O_3
- **Working**
  - Anode : $2O^{2-} \longrightarrow O_2 + 4e^-$
    Cathode : $O_2 + 4e^- \longrightarrow 2O^{2-}$
  - $E_{cell} = \frac{2.303\,RT}{4F} \log \frac{P_1}{P_2}$

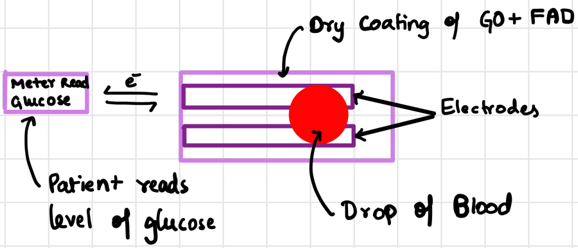
    P_1 → Partial pressure of O_2 in → reference air
    P_2 → Partial pressure of O_2 in → exhaust gas

GLUCOSE SENSOR

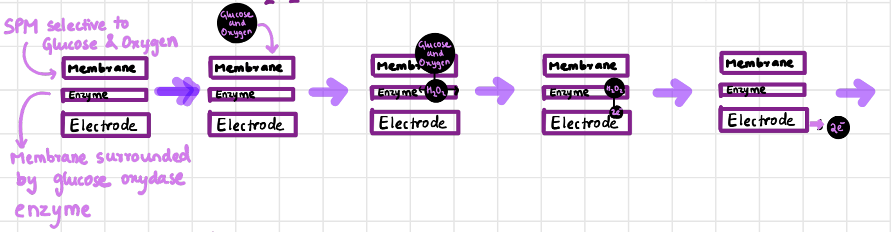
- Used to check concentration of Glucose in blood using glucometer
- Provides quick response if sugar is high (or) low

- We monitor blood glucose to :
  - Reduce risk of diabetes
  - Allow diabetics to see if insulin & other medicines are working
  - Prevent hypoglycemia (or) hyperglycemia

- Glucose Sensor consists
  - Analyte
  - Bio receptor
  - Transducer
  - Electronics & Display



- **Working**
  - Enzyme Glucose oxidase (GOx) catalyze oxidation of glucose by molecular oxygen producing glucolactone & H_2O_2
  - To work as catalyst, GOx requires a redox cofactor - flavin adenine dinucleotide (FAD) which works as initial e^- acceptor & reduced to $FADH_2$
  - Glucose + GOx − FAD$^+$ ⟶ Glucolactane + GOx − $FADH_2$
  - The cofactor is regenerated by reacting with oxygen, leading to formation of H_2O_2
    GOx − $FADH_2$ + O_2 ⟶ GOx − FAD + H_2O_2
  - H_2O_2 oxidised at Pt electrode



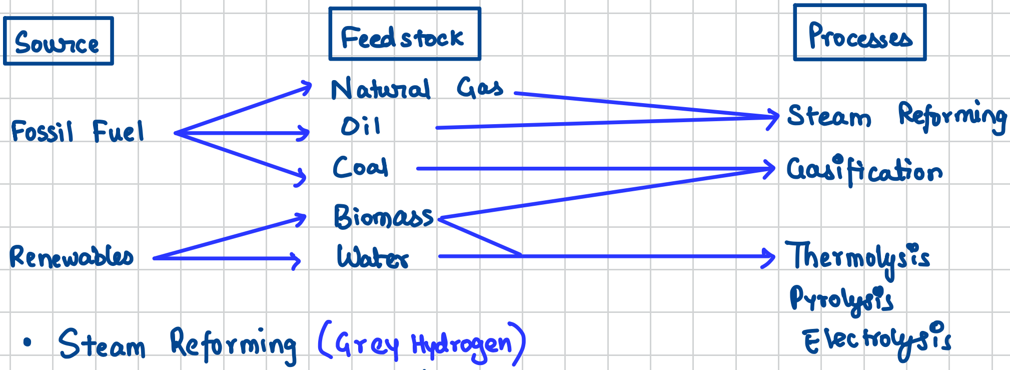
- **Limitations**
  - Extreme environmental conditions (or) medication interferences may effect glucose reading
  - Incorrect reading may lead to treatment errors.

hydrogen storage devices

- Hydrogen Energy
  - It is one of the potential sources of fuel
  - Advantages
    - Abundance in Earth's crust
    - Compatibility of H with fuel cells
    - High Efficiency
  - Disadvantages
    - High cost
    - Highly Flammable
    - Still depends on fossil fuels

- Hydrogen Economy
  - It reduces pollution
  - It is also Carbon - Free

- Hydrogen Production Methods



- Steam Reforming (Grey Hydrogen)
  - Natural gas is used
  - Most widespread process for Hydrogen Generation

- Gasification (Black Hydrogen)
  - Hydrogen produced from coal by gasification
  - Coal $\longrightarrow CO_2 \xrightarrow{\text{gasification}} CO \xrightarrow{\text{water gas shift}} CO_2 + H_2 \xrightarrow{\text{Purified}}$ Pure H_2

- Thermolysis (Green Hydrogen)
  - Water is subjected to thermochemical water splitting at 500-2000°C
  - It is carried in a close system & chemical is reused, water is only consumed and H_2 & O_2 is produced

- Photolysis
  - The process that uses light energy to split water into H_2 & O_2

- Electrolysis
  - Uses electricity to split water into H_2 & O_2 in a unit called Electrolyzer

- Steam Reforming (Steam Methane Reforming)
  - It has 4 Steps
    - Desulpharization
      - Sulphur removal from feedstocks because it can poison catalyst

    - Steam Reforming
      - Steam, Fuel & Air form syngas in reform chamber in presence of catalyst
      - $CH_4 + H_2O + 206\ kJ/mol \longrightarrow CO + 3H_2$
      - 850-900°C, Ni Catalyst, Endothermic r/n, Low pressure required

    - Shift Reforming (Water Gas Shift r/ns)
      - $CO + H_2O \xrightarrow{Fe_3O_4/Cr_2O_3} CO + H_2 + 41\ kJ/mol$
      - 350°C low temp, H_2 has traces of CO as impurities

    - Purification
      - Pure H_2 is formed by removing CO by methanation
        $CO + 3H_2O \longrightarrow CH_4 + H_2O$

  - Advantages -
    - Higher yield of H_2 (50%)
    - Heat generated can be recycled to increase efficiency
    - Relatively Stable Process

  - Disadvantages -
    - Lot of carbon content formed
    - External heat source is required to initiate r/n

- Green Hydrogen
  - Refers to production of H_2 from renewable resources
  - It is done by Electrolysis (Clean Energy & Pollution- Free Electricity)
  - It has 3 methods :
    - Alkaline Electrolysis
    - Proton Membrane Electrolysis
    - High Temperature Electrolysis
  - Working :
    - Water when subjected to electrolysis, uses Electricity for splitting H_2 & O_2 into their gaseous phase
    - The Hydrogen produced by this method is environment friendly as no CO_2 is released
    - Alkaline Water electrolysis is conventional method with simple formation of Hydrogen
    - It requires direct Current (Not AC) supply

  - Gives Low Concentration of water (7 – 10 moles / Lit) as pure water is poor conductor hence acid (H_2SO_4) or base (KOH or $NaOH$) is used to improve conductivity

  - Reactions

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

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

    Overall : $2H_2O + \text{Energy} \longrightarrow 2H_2 + O_2$

  - Advantages
    - No harmful emissions
    - Clean H_2 production
    - No Greenhouse gas produced
    - Used in Fuel Cells
  - Disadvantages
    - High cost
    - Low efficiency
    - High Power Source required
    - Storage is a challenge

Charge Carrier : OH^-

Anode : Ni & its alloys

Cathode : Cd, Pb, Cu, Ag, Pt, Pd

Electrolyte : KOH, NaOH

Catalyst : Ni-Zn, Ni-Co-Au, RuO_2, $LaCoO_3$

- # Hydrogen Storage

- Physical-Based
  - Compressed Gas
  - Cold / Cyro Compressed
  - Liquid H_2
- Material-Based
  - Adsorbent: MOF-5
  - Liquid Organic: BN-methyl cyclopentane
  - Interstitial Hydride: $LaNi_5H_6$
  - Complex Hydride: $NaAlH_4$
  - Chemical Hydrogen: NH_3BH_3

- Liq. H_2 requires cryogenic temperatures because B.P of H_2 is $-252.8°C$ at atmospheric pressure
  - cryogenic → $-150°C$
- Gas. H_2 requires high pressure tanks (350 – 700 bar)
- Solid H_2 can be classified into 2, depending on host's surface
  - Chemisorption – Absorption into surface
  - Physisorption – Adsorption on surface

- Prominent materials for Hydrogen Storage are :

MOF

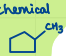
Metal Organic Frameworks

- It is a class of porous materials that have exceptional porosity & tunable pore structures
- Enables High density energy storage of clean fuel gas in MOF adsorbents
- Zn-MOF / MOF-5 is an attractive Hydrogen Storage material cuz balanced gravimetric & volumetric Hydrogen uptake

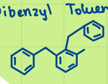
LOHC

Liquid Organic Hydrogen Carriers

- Has great potential for efficient & stable hydrogen storage & transport
- Allows safe & economical large-scale transoceanic transport & storage
- Organic Chemicals that can absorb & release hydrogen through chemical r/ns are - Methyl cyclopentane



and Dibenzyl Toluene



INTERSTITIAL HYDRIDE

- Contain larger quantity of H than same volume of liq. H
- Have advantage in amount of hydrogen on weight basis
- Certain interstitial hydrides are suitable for hydrogen storage & transportation

ex: LiN_5H_6

COMPLEX HYDRIDES

- Composed of metal cations (Li, Mg, Na etc) & Hydrogen containing coordination anions (AlH_4^-, NH_2^-, BH_4^-)
- On heating, metallic hydride decomposes to hydrogen & finely divided metal

ex: $3NaAlH_4 \longrightarrow Na_3AlH_6 + 2Al + 3H_2$

CHEMICAL HYDROGEN

- Hydrogen released from a material thru chemical r/n
- Hydrogen is restored thru chemical r/n when metal is being recharged
- NH_3-BH_3 has exceptional properties for chemical hydrogen gas storage

Liquid Form of Hydrogen

Adv :
- It exists below 20K
- Stored in cryogenic tanks
- Low vol. compressed gaseous H_2

Dis :
- Reinforced & Insulated storage tank req.
- Cooling & Compression process consume energy

Solid Form of Hydrogen

Adv:
- Hydrogen can be released when required by thermal simulation etc.,
- Ease of Handling
- Safety

Dis : Under Research & Development

Gaseous Form of Hydrogen

Adv :
- Less Infrastructure
- Cost effective
- Can be compressed into high pressure in gas form

Dis :
- Needs extra energy
- Large space occupied
- Leak proof tanks required

- Challenges of materials & Solutions
  - All materials used have high specific surface areas but have weak binding forces with Hydrogen (Vander Waals Forces)
  - Lots of research shows that metal decorations increase bonding energy of Hydrogen on sorption-based materials
  - Carbon materials can store more Hydrogen because of Hydrogen spillover phenomenon

Hydrogen Spillover

- Migration of Hydrogen atom from metal surface into non-metal support or absorbent