Module 4 - Energy Devices

Electrochemical and electrolytic cells

- Electrode materials with examples

Electrochemical cell

- Definition, Nernst relation, Daniell cell, numerical problem

Types of Batteries:

- Primary & Secondary Batteries
- Chemistry of Li ion secondary batteries

Fuel Cells:

- H_2-O_2 Fuel Cell (HOFC) and Solid Oxide Fuel Cell (SOFC)

Solar Cells:

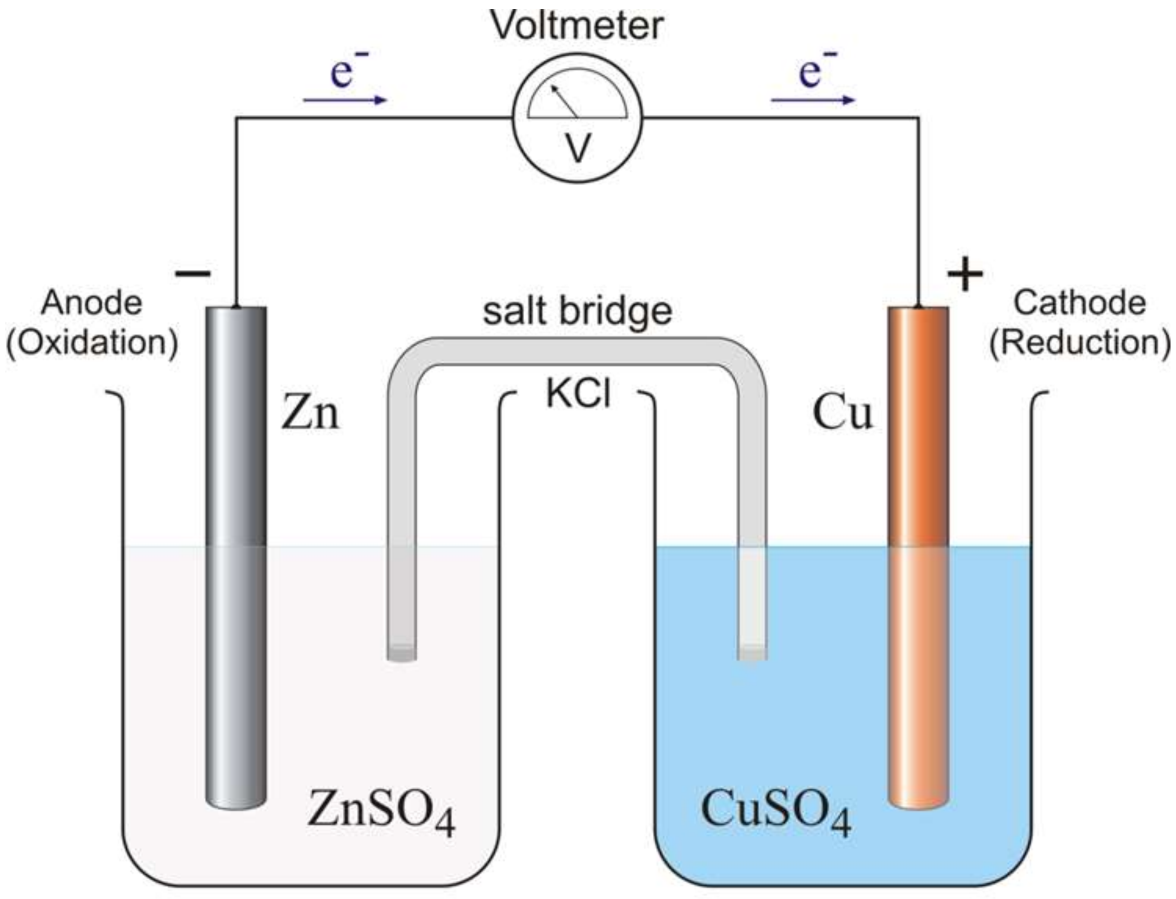
- Semiconductors
- Silicon-based Photo-voltaic Cell
- Photo-electrochemical Cell and
- Dye-sensitized Cell (DSC)

Electrochemical Cell

- A device that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a non-spontaneous redox reaction.
- An electrochemical cell typically consists of
  - Two electronic conductors (also called electrodes >> anode and cathode)
  - An ionic conductor (called an electrolyte)
  - the electron conductor used to link the electrodes is often a metal wire, such as copper wiring
- The electrochemical cells are broadly classified into two types:
  - Galvanic or voltaic cell: Converts the energy released by a spontaneous chemical reaction to electrical energy. $\Delta G < 0$
  - Electrolytic cell: Consumes electrical energy from an external source to drive a non-spontaneous chemical reaction. $\Delta G > 0$

Daniel Cell

- Invented by British chemist John Frederic Daniell.
- Zn Electrode dipped in $ZnSO_4$ solution:
  - **Oxidation:** $Zn \rightarrow Zn^{2+} + 2e^-$
- Cu Electrode dipped in $CuSO_4$ solution:
  - **Reduction:** $Cu^{2+} + 2e^- \rightarrow Cu$
- Each electrode is referred to as half cell which are connected through a salt bridge
- Salt bridge: KCl or NH_4Cl in a gelatine form.
- It maintains the charge balance in the two half cells
- It minimizes or eliminates the liquid junction potential
- Cell emf = 1.1 V



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

$$Zn(s)\,|\,ZnSO_4(aq)\,||\,CuSO_4(aq)\,|\,Cu(s)$$

EMF of Electrochemical Cell

- **The electromotive force (EMF): Maximum potential difference between two electrodes of a galvanic or voltaic cell.**
- **This quantity is related to the tendency for an element, a compound or an ion to acquire (i.e. gain) or release (lose) electrons.**
- **Cell reaction is feasible when E_{cell} has positive value.**
- **Cell EMF in terms of Nernst Equation:**

$$E_{cell} = E^{o}_{Cell} - \frac{0.0595}{2} \log \frac{[Oxid.]}{[Red.]}$$

$$E^{o}_{Cell} = E^{o}_{cathode} - E^{o}_{Anode}$$

1. **Write the half cell reaction, the net reaction and cell EMF of the following cell:**

$Cd | Cd^{2+}$ (0.01 M) $\|$ Cu^{2+} (0.5 M) $| Cu$

The standard reduction potentials are – 0.40 V and 0.34 V respectively.

- The half reactions:

  At anode: $Cd \rightarrow Cd^{2+} + 2e^-$ *Standard reduction potential* = – 0.40 V

  At cathode: $Cu^{2+} + 2e^- \rightarrow Cu$ *Standard reduction potential* = 0.34 V

- Net reaction: $Cd + Cu^{2+} \rightarrow Cu + Cd^{2+}$

$$E^o_{Cell} = 0.34 - (-0.40) = 0.74$$

- *Cell EMF:*

$$E_{cell} = E^o_{Cell} - \frac{0.0595}{2} \log \frac{[Cd^{2+}]}{[Cu^{2+}]}$$

$$= 0.74 - \frac{0.0595}{2} \log \frac{[0.01]}{[0.5]}$$

$$E_{cell} = 0.74 - \frac{0.0595}{2} \log [0.02]$$

$$= 0.74 - \frac{0.0595}{2} \times (-1.698)$$

$$E_{cell} = 0.74 - (-0.050) = 0.74 + 0.05$$

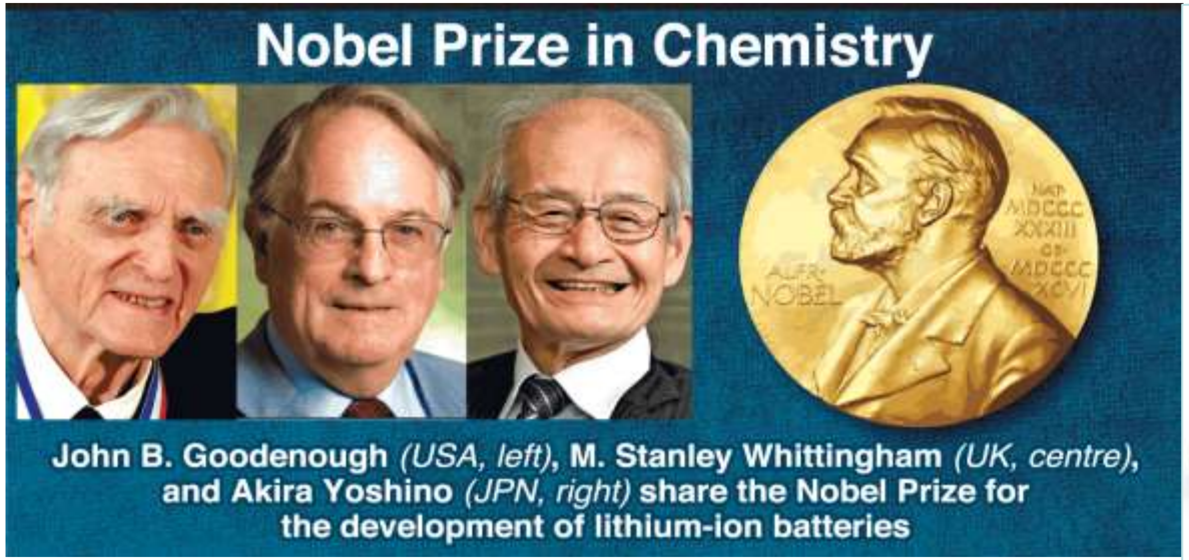
$$E_{cell} = 0.79$$

Batteries

Primary battery	Secondary battery
Electrochemical cell reaction is irreversible	Electrochemical cell reaction is reversible
The reactants cannot be regenerated	The reactants can be regenerated by passing D.C. in the opposite direction to the discharging direction
Disposable after complete discharge; usable for only once.	Reusable after complete or partial discharge.
Cheaper in cost	Expensive than primary batteries
Higher charge density	Lesser charge density
e.g. Carbon-Zinc (dry cell), Alkaline and Lithium cells	e.g. Lead-acid, Ni-Cd, Ni-MH, Lithium-ion rechargeable cells

Lithium-Ion (Li ion) Batteries

- Lithium-ion battery is a secondary battery.
- It does not contain metallic lithium as anode.
- As the name suggests, the movement of lithium ions are responsible for charging & discharging.
- Lithium ion battery technology was first proposed in the 1970s by M Whittingham who used titanium sulphide for the cathode and lithium metal for the anode.
- The Nobel Prize in Chemistry 2019 is awarded to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino.



John B. Goodenough *(USA, left)*, **M. Stanley Whittingham** *(UK, centre)*, **and Akira Yoshino** *(JPN, right)* **share the Nobel Prize for the development of lithium-ion batteries**

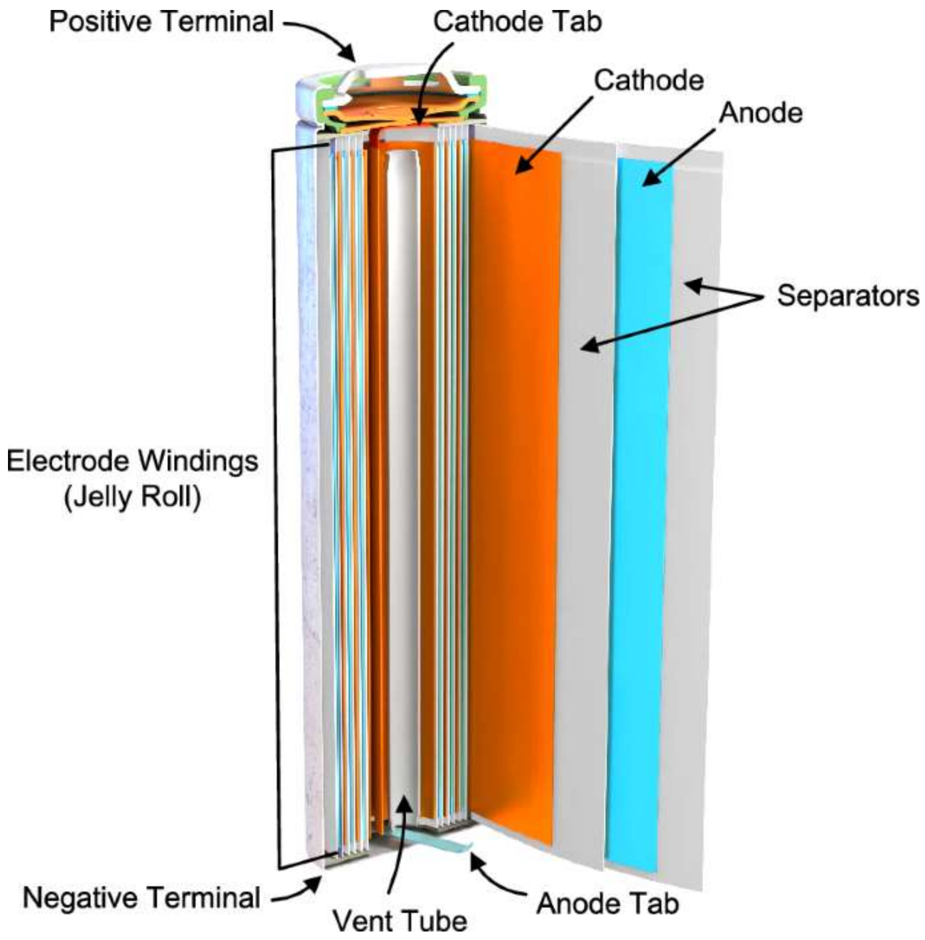
Why lithium?

- **Currently, most portable electronic devices, including cell phones and laptop computers, are powered by rechargeable lithium-ion (Li-ion) batteries, because ???**

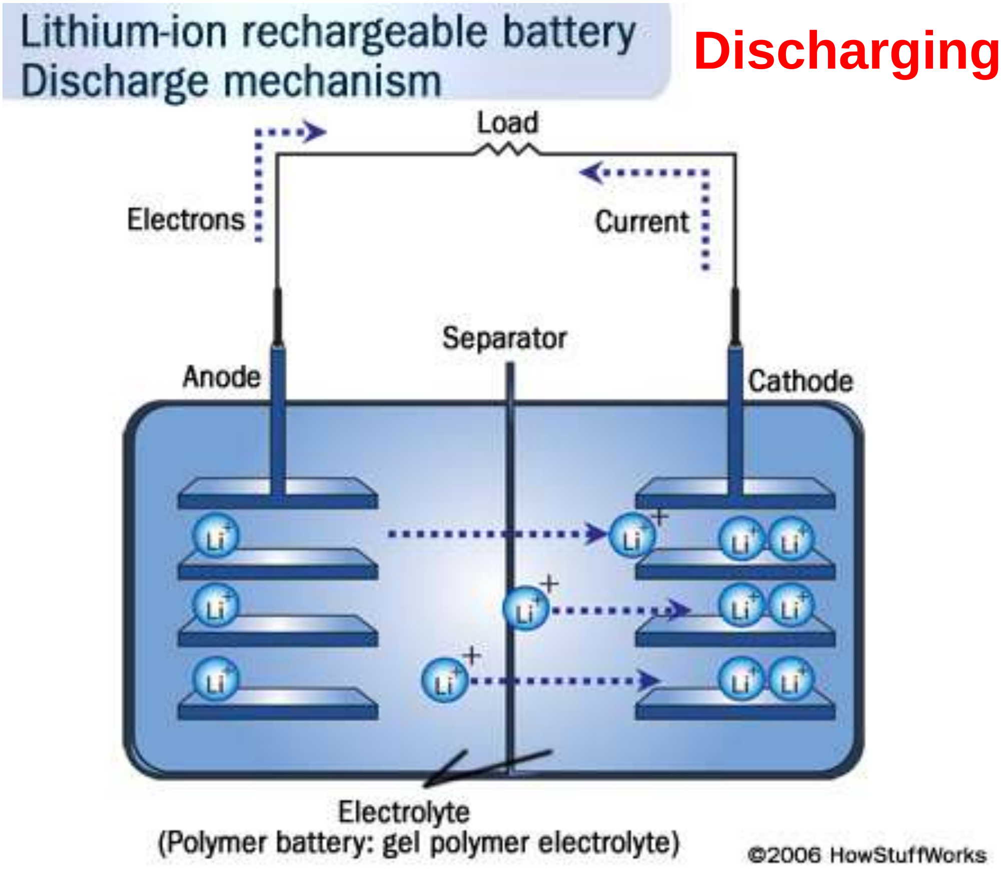
1. **Lithium is a very light element.**
2. Li-ion batteries achieve a **high specific energy density** which is the amount of energy stored per unit mass.
3. Because **Li^+ has a very large negative standard reduction potential**, Li-ion batteries produce a higher voltage per cell than other batteries.
4. A Li-ion **battery produces a maximum voltage of 3.7 V per cell**, nearly three times higher than the **1.3 V per cell that Nickel–Cadmium and Nickel–metal hydride batteries** generate.
5. As a result, a **Li-ion battery can deliver more power than other batteries of comparable size**, which leads to a higher volumetric energy density—the amount of energy stored per unit volume.

Construction of Lithium-Ion (Li ion) Batteries

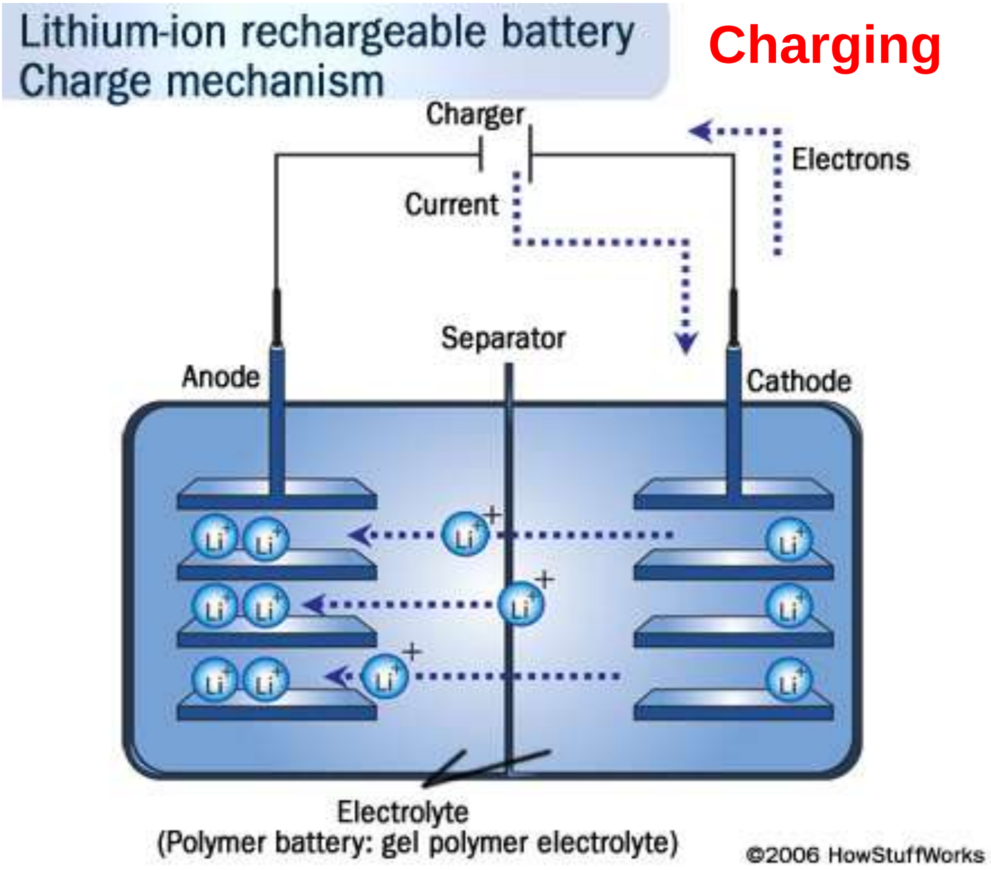
- **Cathode:** This is the positive electrode and it is typically layers of **lithium-metal oxide** ($LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, $LiNiMnCoO_2$) and lithium metal polyanionic materials ($LiFePO_4$, $LiMnPO_4$, $LiFeSO_4F$, etc.).
- **Anode:** The negative electrode is made from **graphite**, usually with composition $Li_{0.5}C_6$.
- **Electrolyte:** Mixture of organic carbonates such as **ethylene carbonate, diethyl carbonate.**
- **Separator:** Prevents touching two electrodes. This absorbs the electrolyte, and enables the passage of ions, but prevents the direct contact of the two electrodes within the lithium in cell.



Charging Reaction and Discharging



Discharging



Charging

The lithium ion moves from the anode to the cathode during discharge and from the cathode to the anode when charging

Anode: lithium adsorbed over the carbon (graphite) material

Cathode: lithium in between the layered CoO_2(Lithium metal oxide)

Charging Reaction and Discharging

Charging Reaction:

- When the cell is being charged, cobalt ions are oxidized and release electrons.
- Simultaneously Li^+ ions migrate out of $LiCoO_2$ and into the graphite.
- Electrons flow from the positive electrode to the negative electrode.
- The electrons and Li^+ ions combine at the negative electrode.

Anode: $LiCoO_2 \rightarrow Li_{1-n}CoO_2 + n\,Li^+ + n\,e^-$

Cathode: $C_6 + n\,e^- + n\,Li^+ \rightarrow Li_nC_6$

$$LiCoO_2 + C_6 \rightarrow Li_{1-n}CoO_2 + Li_nC_6$$

Discharging Reaction:

- Li^+ ions move out of the anode and migrate through the electrolyte where they enter the spaces between the cobalt oxide layers.
- Simultaneously electrons flow through the external circuit.
- Electrons reduce cobalt at ions at the positive electrode to regenerate $LiCoO_2$.

Anode: $Li_nC_6 \rightarrow C_6 + n\,e^- + n\,Li^+$

Cathode: $Li_{1-n}CoO_2 + n\,Li^+ + n\,e^- \rightarrow LiCoO_2$

$$Li_{1-n}CoO_2 + C_6Li_n \rightarrow LiCoO_2 + C_6$$

Chemistry and Construction

- Anode here is a non-metallic compound, e.g. carbon, which can store and exchange lithium ions.
- A lithium ion-accepting material, for example MnO_2 or CoO_2 is then used as the cathode material. Lithium ions are exchanged back and forth between the two electrodes (carbon, graphite) during discharging and charging. Hence, these electrodes are called **intercalation electrodes.**
- This type of battery is known as a “**rocking chair battery**” as the ions simply “rock” back and forth between the two electrodes.

Lithium ion battery variants

NAME	CONSTITUENTS	ABBREVIATION	MAJOR CHARACTERISTICS	APPLICATIONS
Lithium Cobalt	$LiCoO_2$	LCO	High capacity	Cell phones, laptops, cameras
Lithium Manganese Oxide	$LiMn_2O_4$	LMO	Lower capacity	Power tools, medical, hobbyist
Lithium Iron Phosphate	$LiFePO_4$	LFP	Lower capacity	Power tools, medical, hobbyist
Lithium Nickel Manganese Cobalt Oxide	$LiNiMnCoO_2$	NMC	Lower capacity	Power tools, medical, hobbyist
Lithium Nickel Cobalt Aluminium Oxide	$LiNiCoAlO_2$	NCA		Electric vehicles and grid storage

- **Lithium polymer (Poly-Carbon monofluoride) batteries have an output of 2.8 V and moderately high energy density.**

Lithium-ion battery applications

- **Portable power packs:** Li-ion batteries are lightweight and more compact than other battery types, which makes them convenient to carry around within cell phones, laptops and other portable personal electronic devices.
- **Uninterruptible Power Supplies (UPSs):** Li-ion batteries provide emergency back-up power during power loss or fluctuation events to guarantee consistent power supply.
- **Electric vehicles:** As Li-ion batteries can store large amounts of energy and can be recharged many times, they offer good charging capacity and long life spans which creates high demand for Li-ion battery packs for electric, hybrid or plug-in hybrid electric vehicles.
- **Marine vehicles:** Li-ion batteries are emerging as an alternative to gasoline and lead-acid batteries in powering work or tug boats and leisure craft like speed boats and yachts.
- **Personal mobility:** Lithium-ion batteries are used in wheelchairs, bikes, scooters and other mobility aids for individuals with disability or mobility restrictions.
- **Renewable energy storage:** Li-ion batteries are also used for storing energy from solar panels and wind turbines as they can be charged quickly. They are lighter, more compact and can hold higher amounts of energy than lead-acid batteries.

Advantages & Disadvantages of Lithium Ion Battery

Advantages:

- **High energy density:** High energy density is one of the biggest advantages of lithium ion battery technology. This higher power density offered by lithium ion batteries is a great advantage for their use in electronic gadgets and electric vehicles.
- **Low self-discharge:** Lithium ion cells is that their rate of self-discharge is much lower than that of other rechargeable cells such as Ni-Cd and NiMH forms.
- **Low maintenance:** Lithium ion batteries do not require active maintenance.
- **High cell voltage:** The voltage produced by each lithium ion cell is about 3.6 volts. This ensure less number of cells in many battery applications.
- **Variety of types available:** There are several types of lithium ion cell available. This ensures the right technology can be used for the particular application needed.
- **No requirement for priming:** Lithium ion batteries are supplied operational and ready to go.
- **Load characteristics:** These provide a reasonably constant 3.6 volts per cell before falling off as the last charge is used.

Disadvantages:

- **Protection required:** Lithium ion cells and batteries are not as robust as some other rechargeable technologies. They require protection from being over charged and discharged too far.
- **Ageing:** Lithium ion batteries suffer from ageing. Often batteries will only be able to withstand 500-1000 charge discharge cycles before their capacity falls.
- **High Cost:** A major lithium ion battery disadvantage is their cost. Typically they are around 40% more costly to manufacture than Nickel cadmium cells.
- **Chances of explosion:**
  - **Bad design or manufacturing defects:** In that case, there wasn't enough space for the electrodes and separator in the battery. When the battery expanded a little as it charged, the electrodes bent and caused a short circuit.
  - **Overcharging:** When overcharged, lithium cobalt oxide releases oxygen which can react with flammable electrolyte leading to overheating.
  - **Electrolyte breakdown:** On overheating, Dimethyl carbonate (electrolyte) decompose to form CO_2 which causes pressure build up in battery, resulting in a dangerous explosion.

What is a Fuel Cell?

A fuel cell is a device that converts chemical energy by combining hydrogen and oxygen into electrical energy, water, and heat through electrochemical reactions

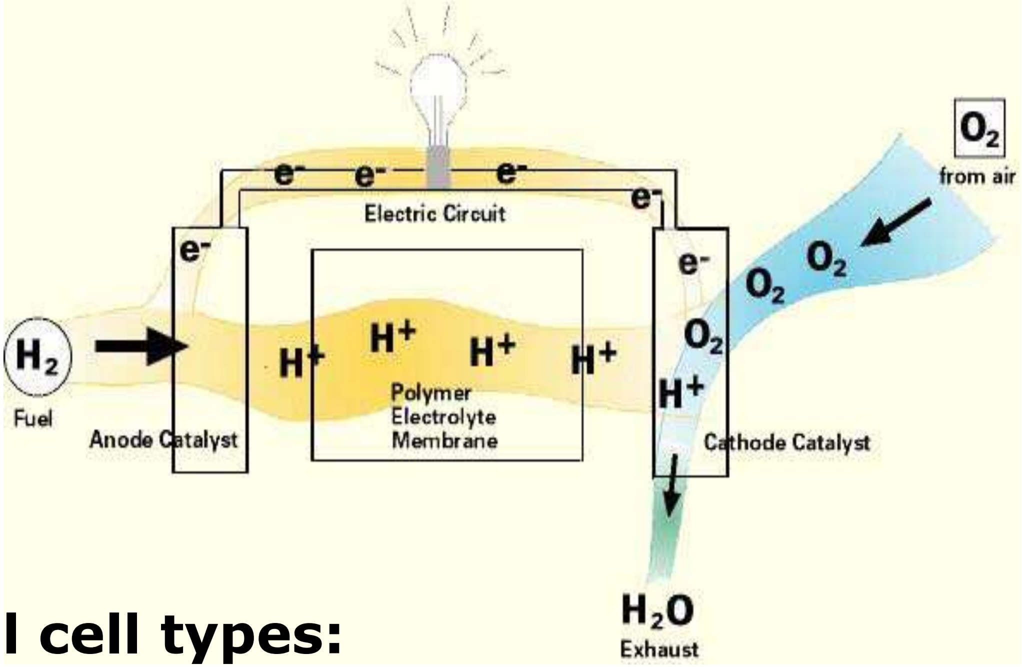
Fuel + O_2 → Oxidation products + Electricity

Importance of fuel cell technology

- Since **conversion of the fuel to energy** takes place via an electrochemical process and not by combustion

- It is a **clean, quiet and highly efficient process** – two to three times more efficient than fuel burning.

Working of a Fuel Cell



The voltage generated by a single cell is typically rather small (< 1 volt), so many cells are connected in series to create a useful voltage.

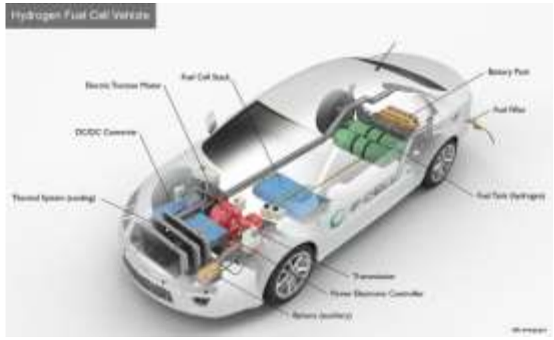
Anode: $2H_2 \rightarrow 4H^+ + 4e^-$

Cathode: $O_2 + 4e^- \rightarrow 2O^{2-}$

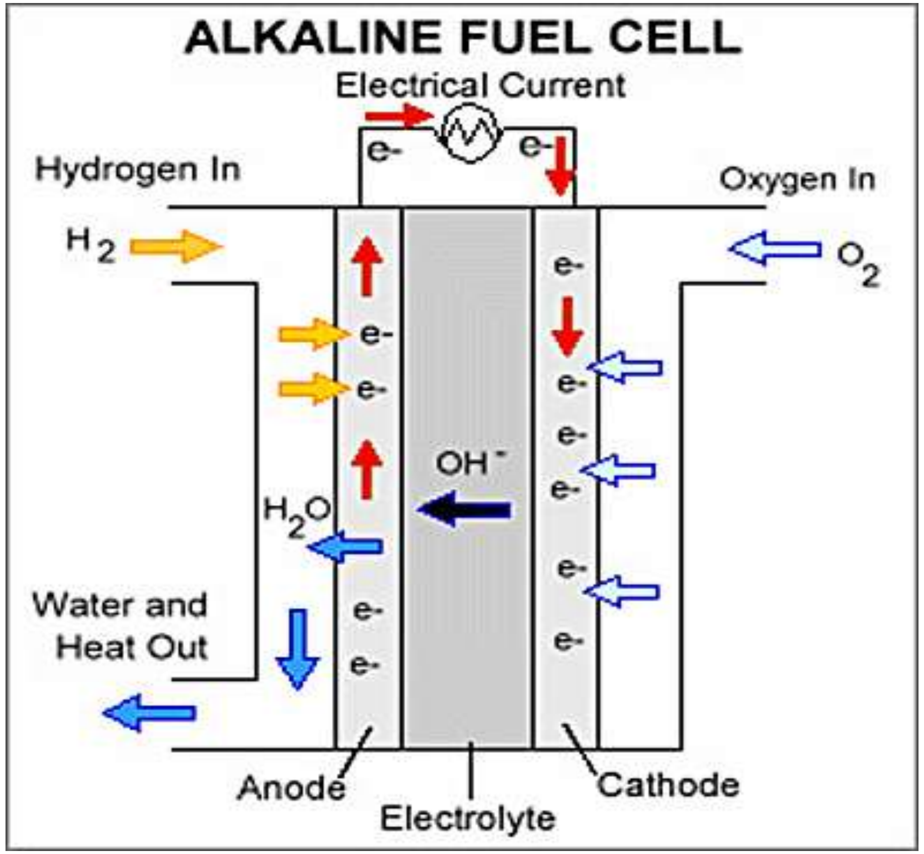
Overall: $2H_2 + O_2 \rightarrow 2H_2O$

Fuel cell types:

- Hydrogen – oxygen fuel cell (HOFC) or alkaline fuel cell
- Polymer electrolyte membrane (PEM) fuel cell
- Solid oxide fuel cell (SOFC)



1. Hydrogen – oxygen fuel cells (HOFC) or alkaline fuel cells (AFCs)



Materials used:

Anode: inert and porous graphite electrode + finely divided Platinum catalyst

Cathode: inert and porous graphite electrode + finely divided Platinum catalyst

Electrolyte: 25% KOH hot solution (alkaline).

Chemistry: H_2 and pure O_2 gases are bubbled through the anode and cathode respectively, and the fuel cell produces power through a red-ox reaction between H_2 and O_2.

At anode (-): $2\ H_{2\ (g)} + 4\ OH^-_{(aq)} \rightarrow 4\ H_2O_{\ (l)} + 4\ e^-$ **(oxidation)**

The electrons flow through an external circuit and enter the cathode.

At cathode (+): $O_{2\ (g)} + 2\ H_2O_{\ (l)} + 4\ e^- \rightarrow 4\ OH^-_{\ (aq)}$ **(reduction)**

Net reaction: $O_{2\ (g)} + 2\ H_{2\ (g)} \rightarrow 2\ H_2O_{\ (l)}$

The standard EMF of the cell: $E^o = E^o_{ox} + E^o_{red}$ = 0.83 V + 0.40 V = 1.23 V.
By stacking a number of cells together in as series to make a battery, the required voltage to drive a motor is achieved.

Electrode specifications:

(i) must be good conductors;
(ii) must be good electron sink;
(iii) must not be consumed or deteriorated by the electrolyte heat or electrode reactions.

Advantages:

- AFCs consume H_2 and pure O_2 producing water, heat, and electricity.
- Efficiency is around 70%, highest among the fuels cells used at present.
- **Operating temperature are 150 to 200°C** suitable for automobile applications.
- **For low-temperature (-54°C to 72°C)** operation, potassium thiocyanate (KSCN) dissolved in liq. NH_3 is used.

Disadvantages:

- Require pure H_2 and O_2 fuel;
- Platinum electrodes used as catalyst are expensive;
- As the electrolyte is aqueous medium, it may leak.

Applications:

Compared to conventional energy generators, **fuels cells occupy less space and weight** and hence used as auxiliary energy source in **space vehicles, submarines**, etc;

In case of H_2/O_2 fuel cells, the **water obtained as product** is a **valuable source of fresh water for the astronauts**.

Fuel cell poisoning:

AFCs can become **poisoned if the oxygen is contaminated with CO_2** resulting in the **conversion of aq. KOH into K_2CO_3**.

Hence, AFCs require the supply of pure O_2 thereby increasing the cost.

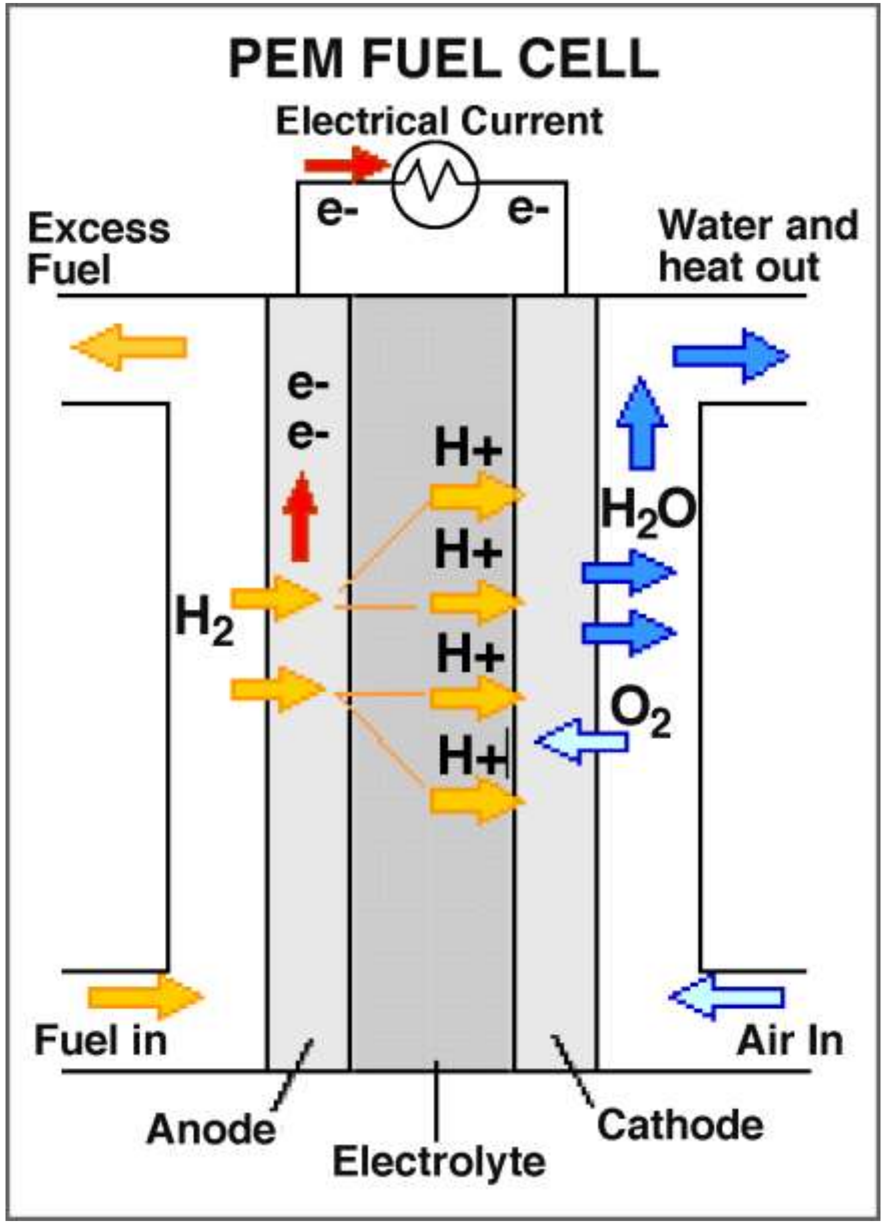
The main mechanisms of poisoning is the change in electrolyte composition from aq. KOH to aq. K_2CO_3 leading to subsequent decrease in ionic conductivity of the electrolyte.

The poisoning effect can be reversed by replacing the poisoned electrolyte with aq. KOH which returns the cell back to its original output.

2. Proton-Exchange Membrane Cell

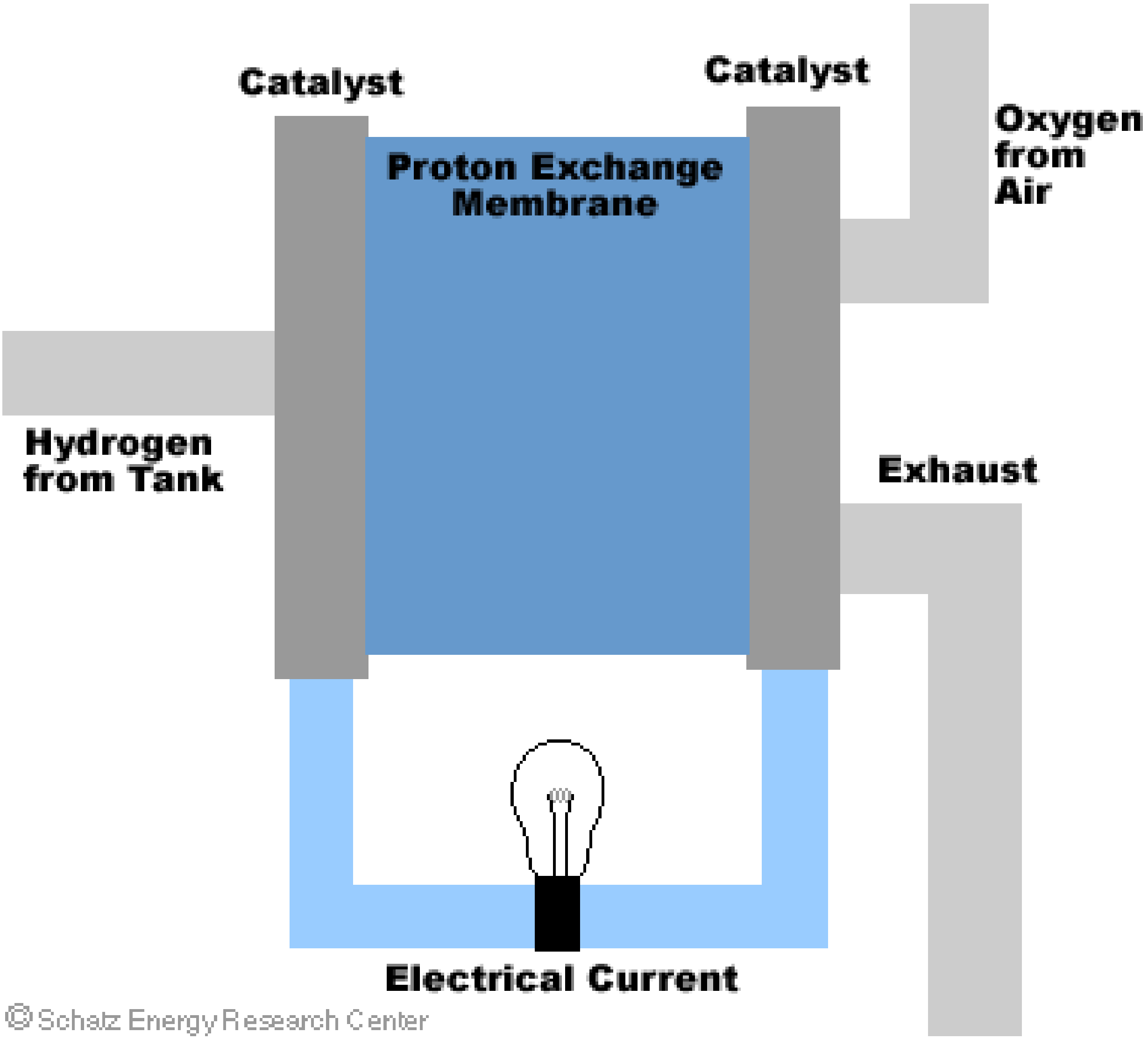
How a fuel cell works:

- In the **polymer electrolyte membrane (PEM) fuel cell, also known as a proton-exchange membrane cell**, a catalyst in the anode separates hydrogen atoms into protons and electrons.
- The membrane in the center transports the protons to the cathode, leaving the electrons behind. The electrons flow through a circuit to the cathode, forming an electric current to do useful work.
- In the cathode, another catalyst helps the electrons, hydrogen nuclei and oxygen from the air recombine.
- When the input is pure hydrogen, the exhaust consists of water vapor. In fuel cells using hydrocarbon fuels the exhaust is water and carbon dioxide.
- Cornell's new research is aimed at finding lighter, cheaper and more efficient materials for the catalysts and membranes.



http://www.news.cornell.edu/releases/Nov03/Fuelcell.institute.deb.html

Polymer - membrane fuel cell



Anode: inert and porous graphite electrode + finely divided Platinum catalyst

Cathode: inert and porous graphite electrode + finely divided Platinum catalyst

Electrolyte: proton-conducting polymer membrane

Anode: $2H_{2(g)} \text{----->} 4H^+_{(aq)} + 4e^-$

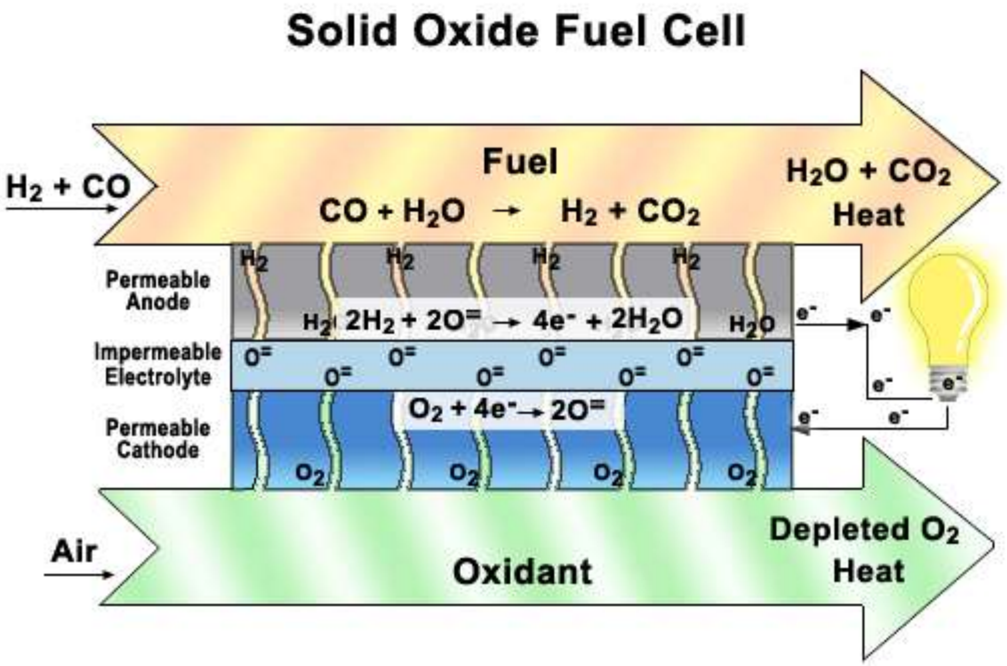
Cathode: $O_{2(g)} + 4H^+_{(aq)} + 4e^- \text{---->} 2H_2O_{(l)}$

3. Solid Oxide Fuel Cells

- The Solid Oxide Fuel Cell (SOFC) uses a **ceramic solid-phase electrolyte** which **reduces corrosion** considerations and **eliminates the electrolyte management problems** associated with the liquid electrolyte fuel cells

- To achieve adequate **ionic conductivity** in such a ceramic, however, the system must **operate at about 1830 ^oF**

- At that temperature, the heat generated can be utilized for **conventional thermal electricity generation** to yield excellent fuel efficiency.



Anode: $2H_2 \rightarrow 4H^+ + 4e^-$

Cathode: $O_2 + 4e^- \rightarrow 2O^{2-}$

Overall: $2H_2 + O_2 \rightarrow 2H_2O$

- It consists of three components - a **cathode**, an **anode**, and an **electrolyte** sandwiched between the two.
- Oxygen from the air flows through the cathode
- A fuel **gas containing hydrogen**, such as **methane**, flows past the anode.
- Negatively charged oxygen ions migrate through the electrolyte membrane react with the hydrogen to form water.
- This electrochemical reaction generates electrons, which flow from the anode to an external load and back to the cathode,
- a final step that both completes the circuit and supplies electric power.
- To increase voltage output, several **fuel cells are stacked** together to form the heart of a clean power generator.

Principle of operation:

- SOFC is made up of all-solid four layers among which the anode, cathode and electrolyte are all made from ceramics, and inter-connect are made up of metal alloys.
- The ceramics used in SOFCs become electrically and ionically active at very high temperature (500 to 1,000°C).
- At high temperatures, reduction of oxygen into oxygen ions occurs at the cathode (air electrode).
- These O^{2-} ions diffuse through the electrolyte to the anode (fuel electrode) where they electrochemically oxidize the fuel gas containing hydrogen.
- In this reaction, a water byproduct is given off as well as electrons. These electrons then flow through an external circuit creating electricity. The cycle then repeats as those electrons enter the cathode material again.
- Reforming natural gas or water gas (H_2 + CO) to extract the necessary hydrogen can be done within the fuel cell thereby eliminating the need of the external reformer. In such a fuel cell, reformate gas (H_2 + CO) is used as a fuel and oxygen as the oxidant.

SOFC design: Thermal expansion due to high temperature operation requires a uniform and well-regulated heating process at startup.

SOFC stacks with **planar geometry design** require an hour to be heated to operational temperature. But, **micro-tubular fuel cell design** requires just a few minutes for the startup.

Characteristics: They operate at very high temperatures (500 to 1,000°C) and hence do not require expensive platinum catalyst material for the redox reaction.

SOFCs are **not vulnerable to carbon monoxide catalyst poisoning** but are **vulnerable to sulfur poisoning**.

Hence, sulfur must be removed before entering the cell through the use of adsorbent beds.

Power output = 100 W to 2 MW. Theoretical efficiency of a SOFC device can exceed 60 %.

In applications designed to capture and utilize the system's waste heat, the efficiency could reach 80 to 85%.

Advantages: high efficiencies, long term stability, fuel flexibility, low emissions, and cost.

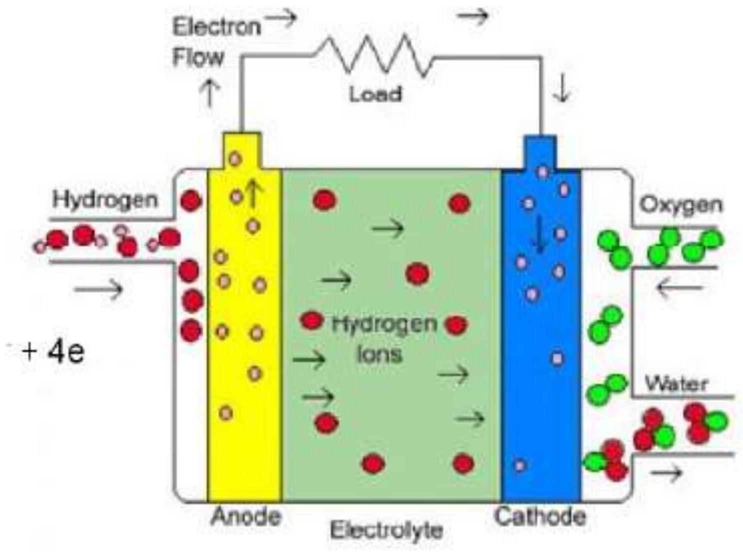
It produces exhaust gases at temperature ideal for combined-cycle electric power plants.

Disadvantages: high operating temperature (500 to 1,000°C) which results in longer start up times and mechanical/chemical compatibility issues.

Fuel Cell Vs. Battery

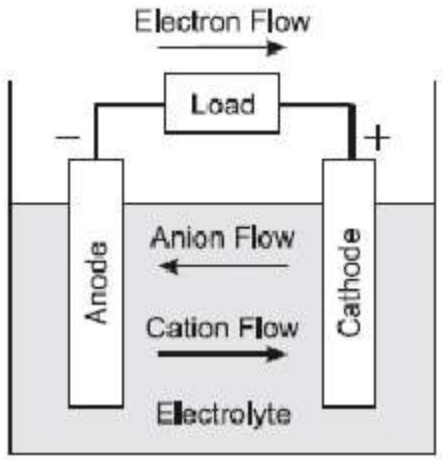
Basic operating principles of both are very similar, but there are several intrinsic differences.

Hydrogen fuel cell



- Thermodynamically Open system
- Platinum coated anode and cathode are gases in contact with a platinum catalyst
- Reactants are externally supplied no recharging required. A fuel cell vehicle is refueled instead of recharged

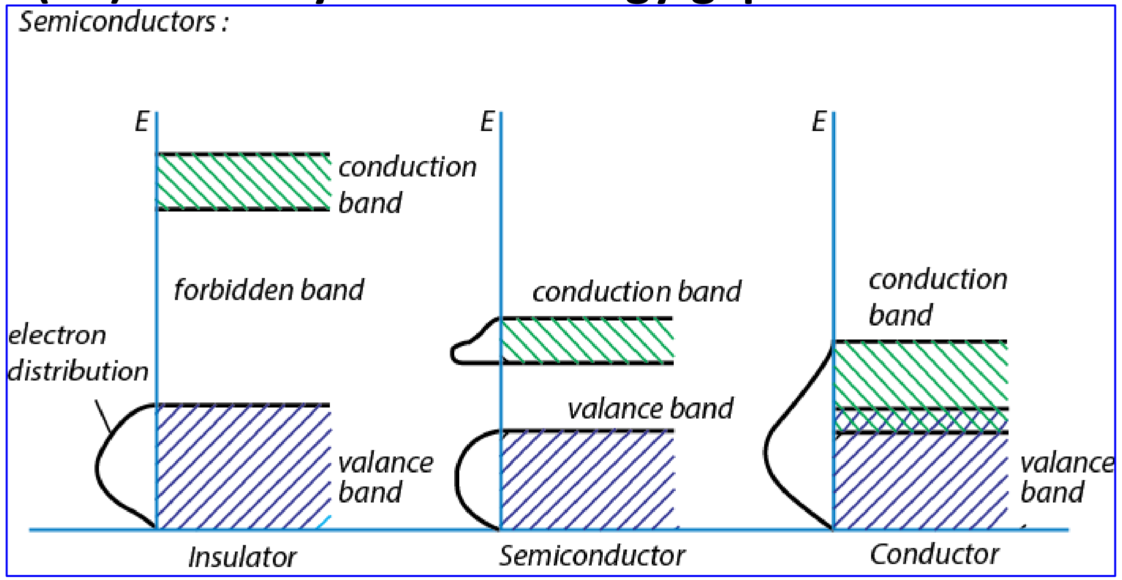
Galvanic cell (battery)



- Thermodynamically Closed system
- Anode and cathode are metals.
- Reactants are internally consumed, need periodic recharging.

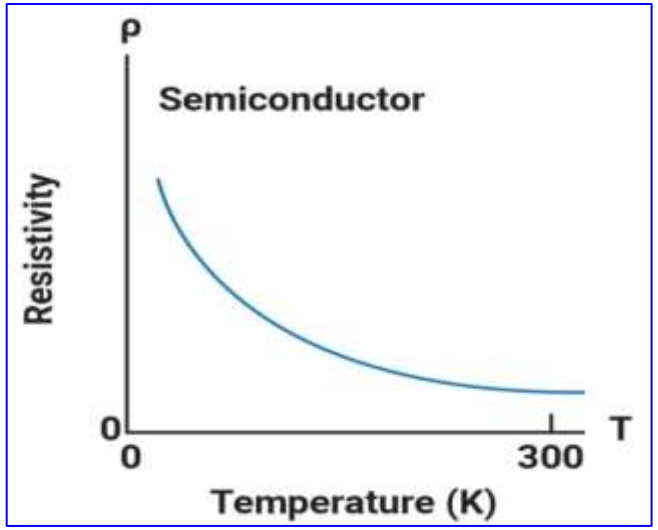
Semiconductors: A semiconductor is usually a solid chemical element that can conduct electricity only under some conditions, making it a good medium for controlling current.

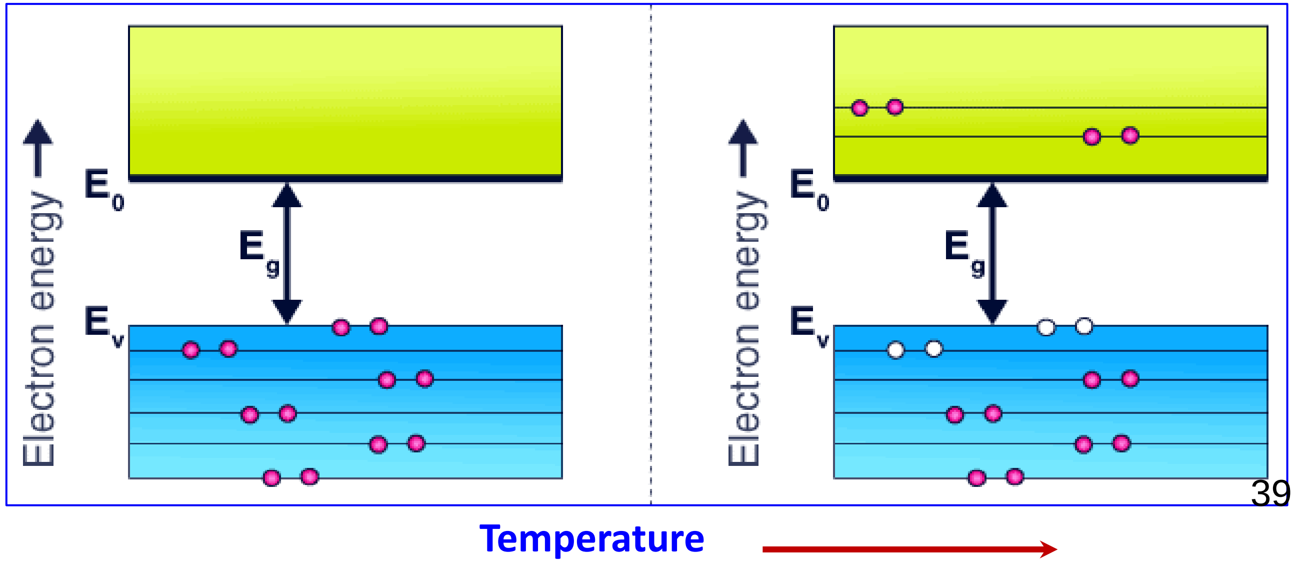
- It has almost filled Valence Band (VB), empty Conduction Band (CB) and very narrow energy gap i.e. of the order of 1 eV.
- Energy gap of Si and Ge semiconductors are 1.0 and 0.7 eV.



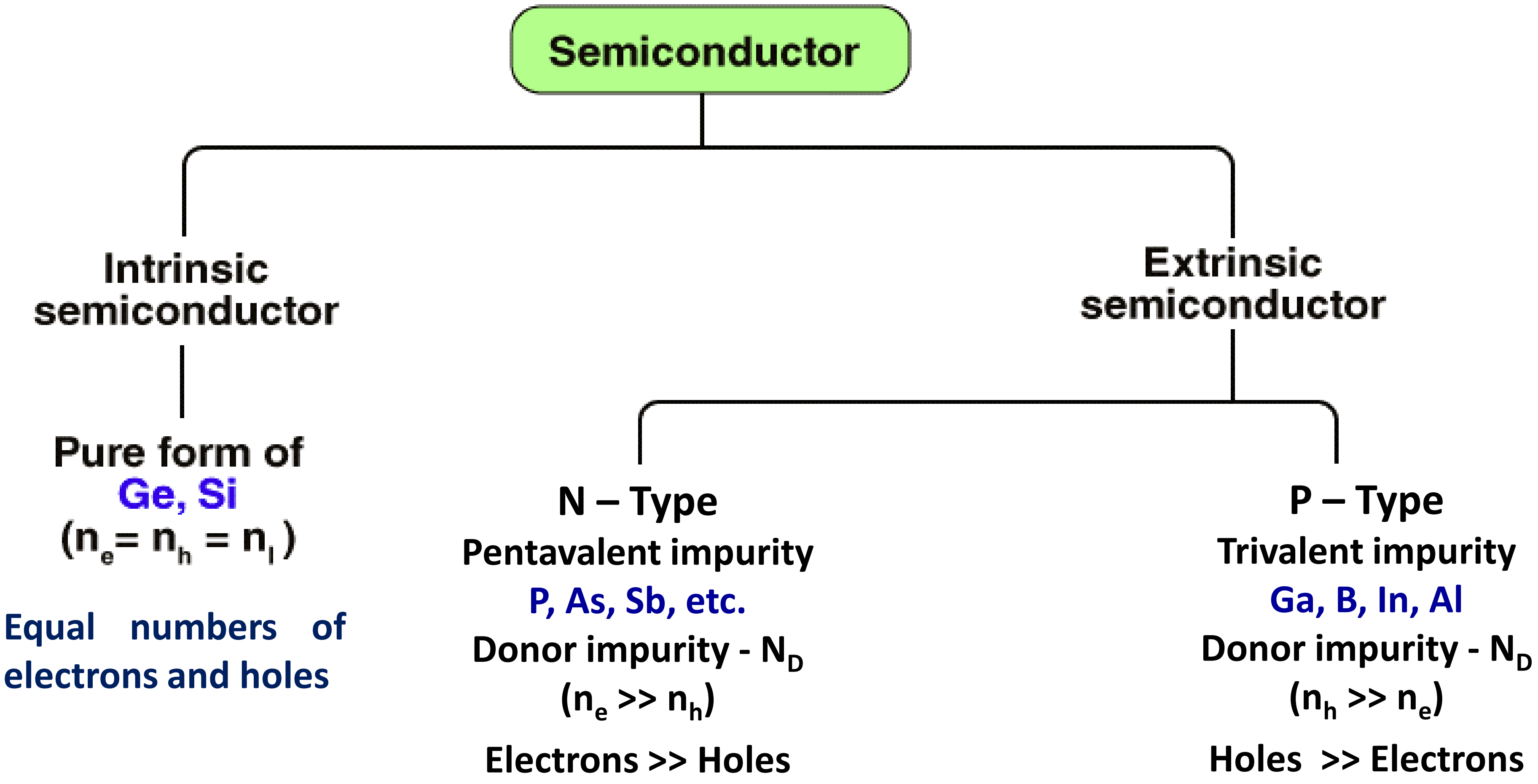
Effect of temperature on conductivity of semiconductors:

- At 0 K (-273 °C), electrons freeze at valence band and hence all semiconductors are insulators.
- Electrical conductivity of semiconductor increases with increasing temperature.
- At higher temperature, transition from VB to CB gets facilitated → higher conductivity or lower resistivity.





Types of semiconductors



Semiconductor

Intrinsic semiconductor

Pure form of
Ge, Si
($n_e = n_h = n_i$)

Equal numbers of electrons and holes

Extrinsic semiconductor

N – Type
Pentavalent impurity
P, As, Sb, etc.
Donor impurity - N_D
($n_e >> n_h$)

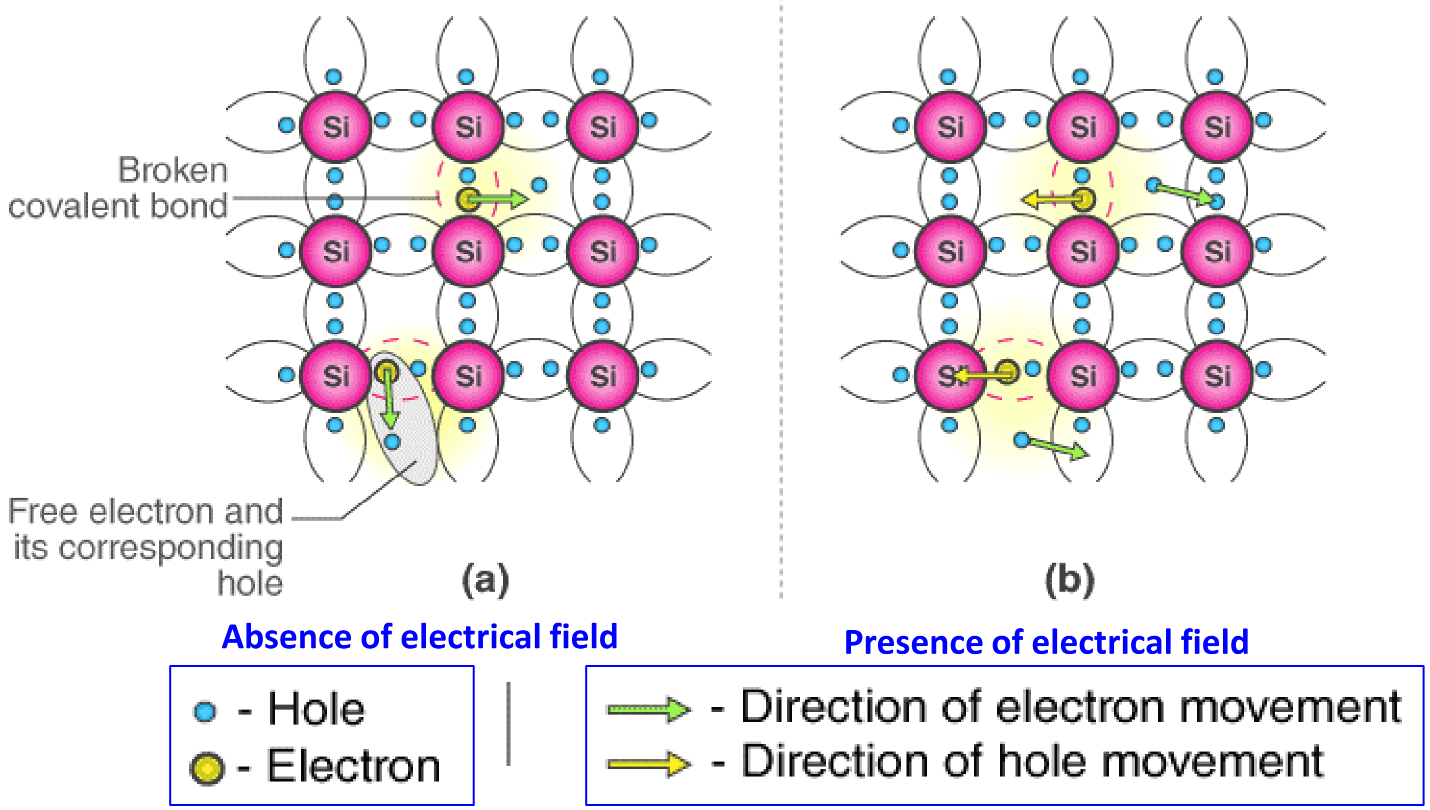
Electrons >> Holes

P – Type
Trivalent impurity
Ga, B, In, Al
Donor impurity - N_D
($n_h >> n_e$)

Holes >> Electrons

- Ge and Si are the most common elemental semiconductors.
- InSb and GaSb (Indium and Gallium antimonides), InAs and GaAs (Indium and Gallium arsenides), GaP (Gallium phosphide), SiC (silicon carbide) and GaN (Gallium nitride) compounds are example for semiconductors.

Intrinsic Semiconductor is chemically very pure but with poor conductivity.
It has equal numbers of negative carriers (electrons) and positive carriers (holes).

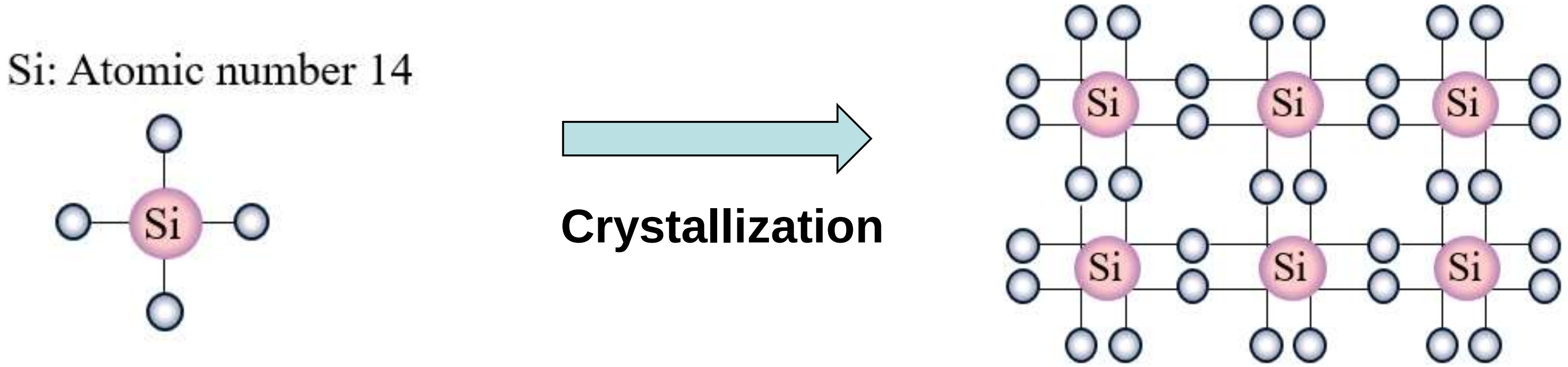


Absence of electrical field

Presence of electrical field

Extrinsic Semiconductor is an improved intrinsic semiconductor with a small amount of impurities added by a process known as "**doping**", which alters the electrical properties of the semiconductor and improves its conductivity.

- Doping process produces two groups of semiconductors:
    - Negative charge conductor (**n-type**) & Positive charge conductor (**p-type**)

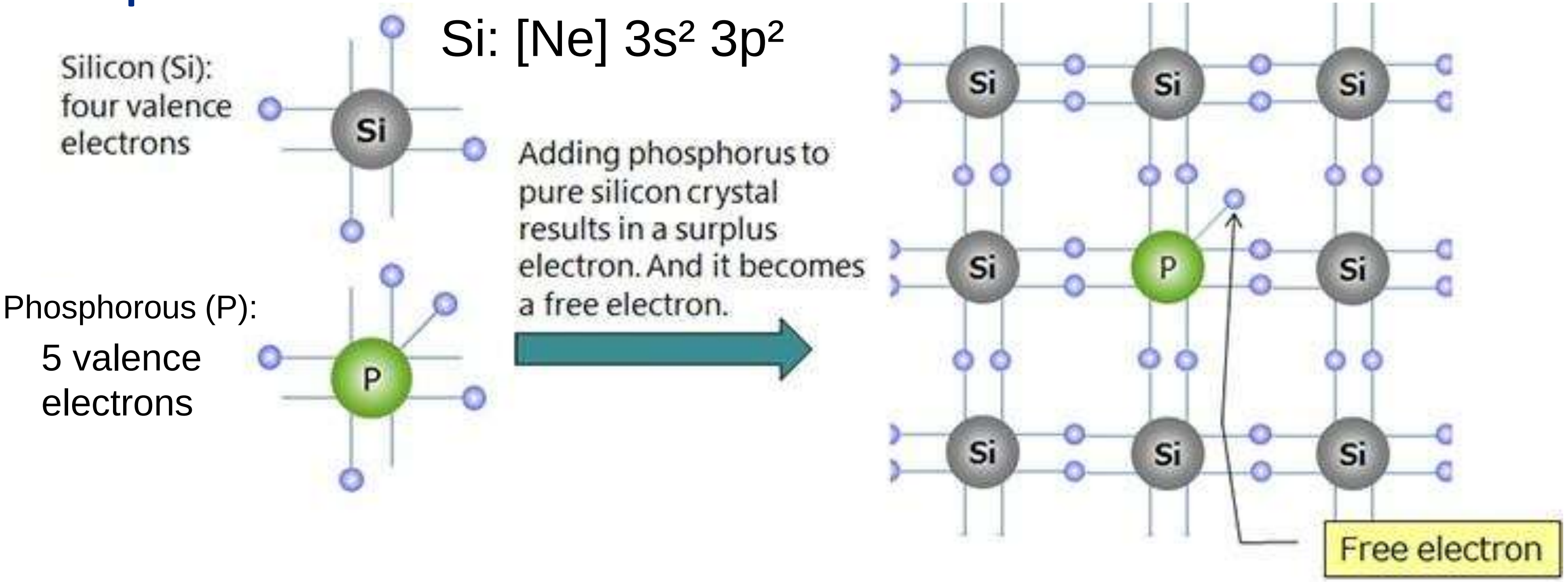

Si: Atomic number 14

Crystallization

n-type Semiconductor: **An n-type semiconductor is an intrinsic semiconductor doped with pentavalent impurity such as P, As, Sb, etc.**

If a small amount of Phosphorus is added to pure Si crystal, one of the valence e^- of Phosphorus becomes free to move around as a surplus electron.

Si: [Ne] $3s^2\ 3p^2$


Silicon (Si): four valence electrons

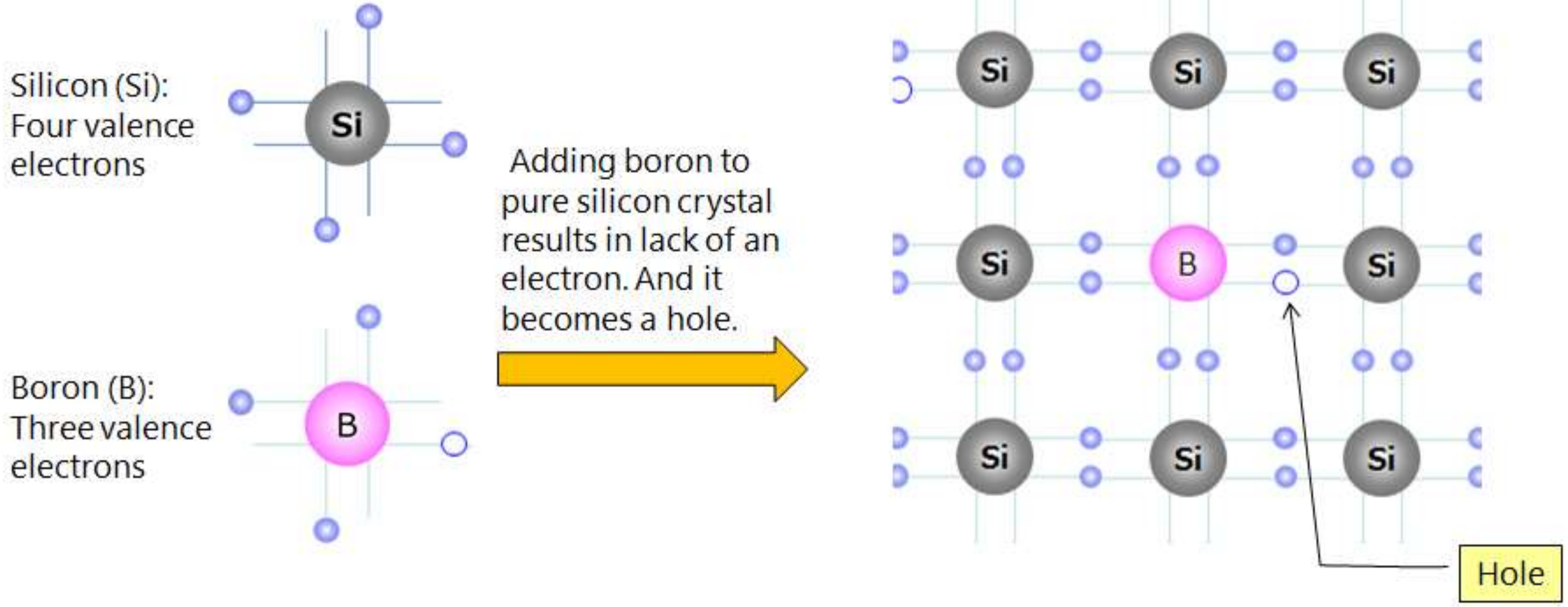
Phosphorous (P): 5 valence electrons

Adding phosphorus to pure silicon crystal results in a surplus electron. And it becomes a free electron.

Free electron

p-type Semiconductor: An p-type semiconductor is an intrinsic semiconductor doped with trivalent impurity such as B, Al, In, etc.

If a small amount of Boron is added to pure Si crystal, valence electrons will be insufficient at one position to bond Si and Boron, resulting in holes that lack electrons.



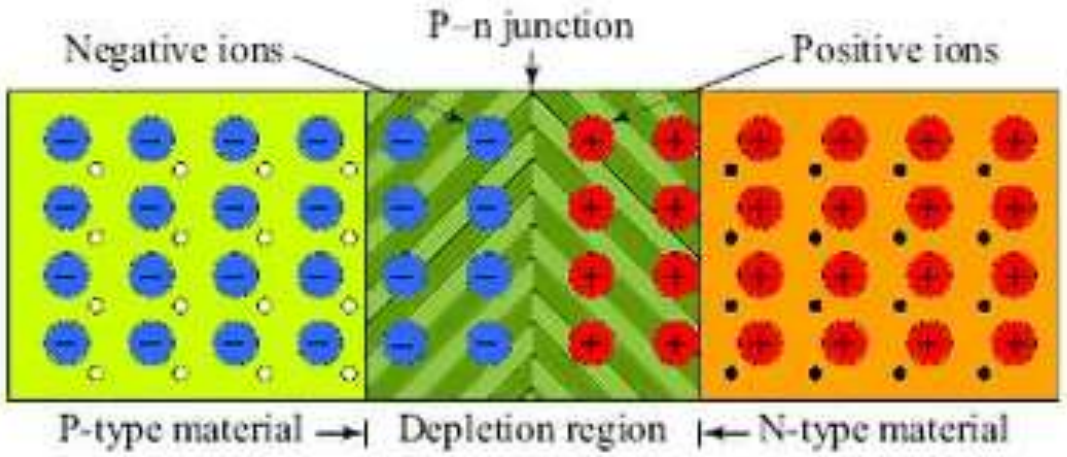
Silicon (Si):
Four valence
electrons

Boron (B):
Three valence
electrons

Adding boron to
pure silicon crystal
results in lack of an
electron. And it
becomes a hole.

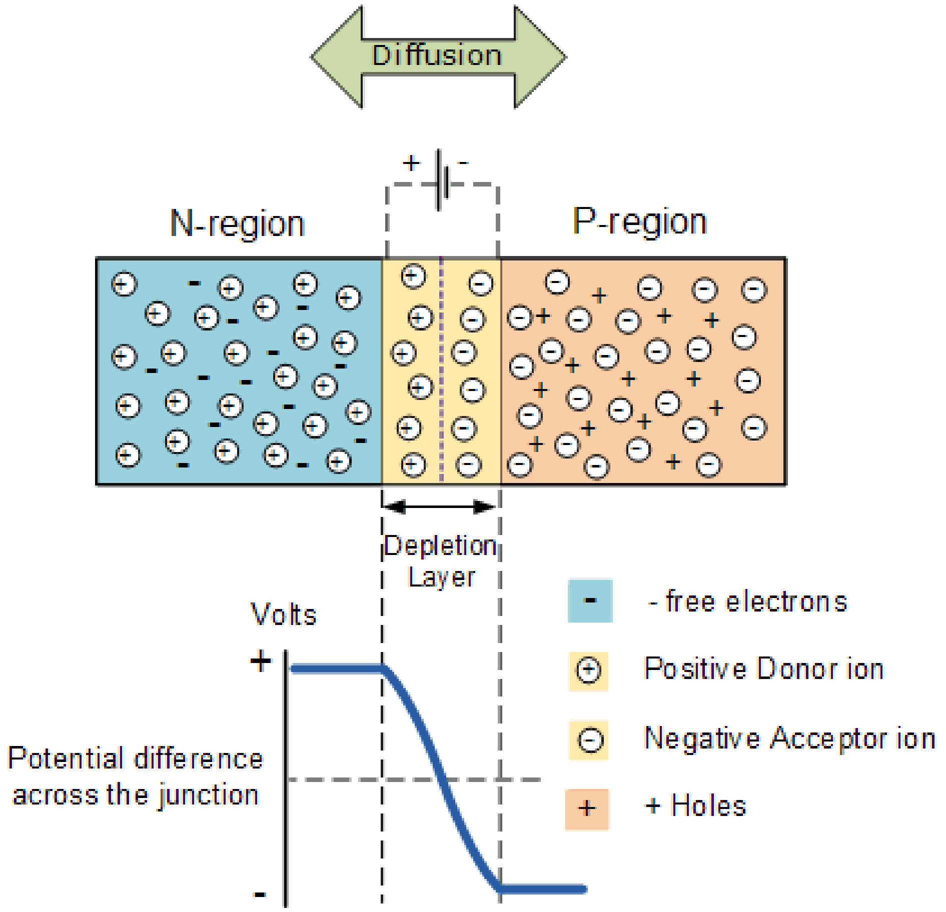
P-N junction is formed when an P-type material is fused together with a N-type material creating a semiconductor diode.

- The P-region contains an excess of holes and the N-region contains an excess of electrons in the outer shells of atoms within the semiconductor.



- The middle portion of the crystal where these p- and n-type semiconductors meet to form a typical junction is known as **P-N junction.**
- As **the pentavalent impurity** atoms in N-type material donate the extra electron in their outermost orbital to the semiconductor crystal (through diffusion), the pentavalent impurity is called **donor impurity** (to form positively charged ions).
- *The free electrons in the n-type region will migrate first to the p-type region than the free electrons in the n-type region away from the junction.* ***This makes a layer of static positive ions in the n-type region adjacent to the junction.***
- The donated electrons will combine with holes from P-type material, also called as **acceptor impurity** (to form negative ions).
- *As the acceptor impurity atoms nearer the junction in the p-type region become negative ions,* ***there will be a layer of negative static ions in p-region adjacent to the junction.***

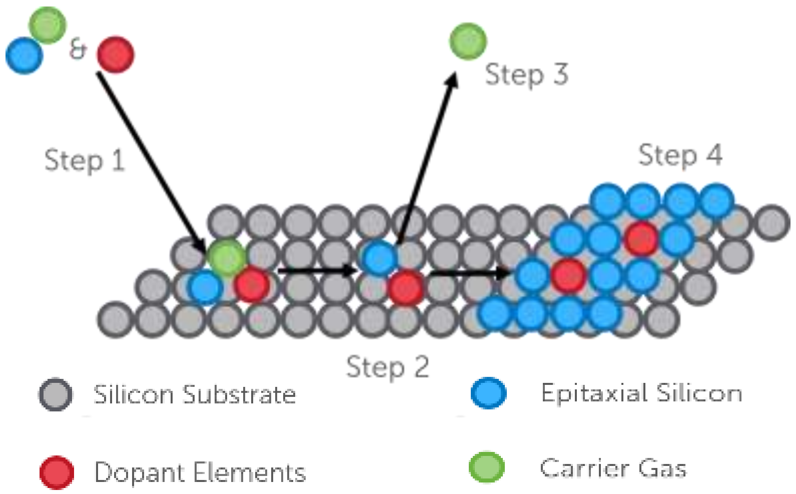
- *After the formation of the sufficiently thick positive ions layer in the n-type region and negative ions layer in the p-type region, no more diffusion of electrons from n-type region to p-type region will happen because there is a negative wall in front of free electrons.* These both layers of ions from the **P-N junction.**
- As one layer is –ve charged and other is +ve charged, there will be an electrical potential across the junction, and the **junction behaves like a potential barrier.**
- *Barrier potential depends on semiconductor material, doping amount and temperature.*
- *Barrier potential for Ge and Si semiconductors are 0.3 and 0.7 V, respectively at 25 °C.*
- ***This potential barrier does not contain any free electron or hole.*** *Since all free electrons are combined with holes in this region, there is depletion of charge carriers (electrons or holes) in this region and hence called as* ***depletion region****.*
- ***The thickness of depletion layer is very tiny in the range of μm.***



Doping techniques

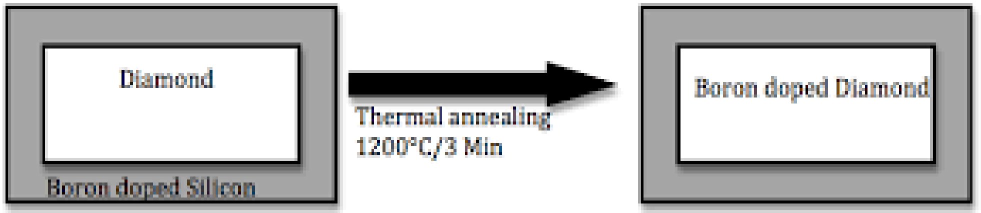
(a). Epitaxy involves controlled deposition of a thin crystal + dopant mixture on another crystalline substrate. The overlayer is called an epitaxial film or epitaxial layer.

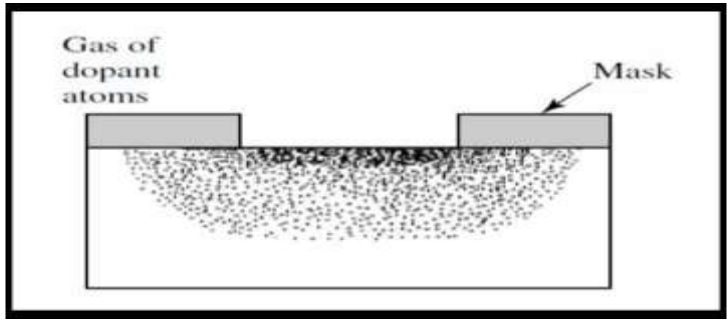
- Si or Ge wafer placed in a long cylindrical quartz tube reactor is heated (by RF induction coil). Then, Ge or Si gases mixed with calculated amount of dopant is passed over the substrate.
- For getting Si epitaxial film, $SiCl_4$, H_2 and N_2 mixture is used.
- For **n-type doping** ⇒ above mixture is used with **phosphine (PH_3).**
- For **p-type doping** ⇒ above mixture is used with **diborane (B_2H_6).**



(b). Diffusion technique involves diffusion of solid or gaseous dopant impurity into the crystal lattice of the semiconductor material without any melting and it consists of heating a P-type dopant..

- By this technique, the extent of impurity atoms penetration can be controlled to less than a few millions of a cm.

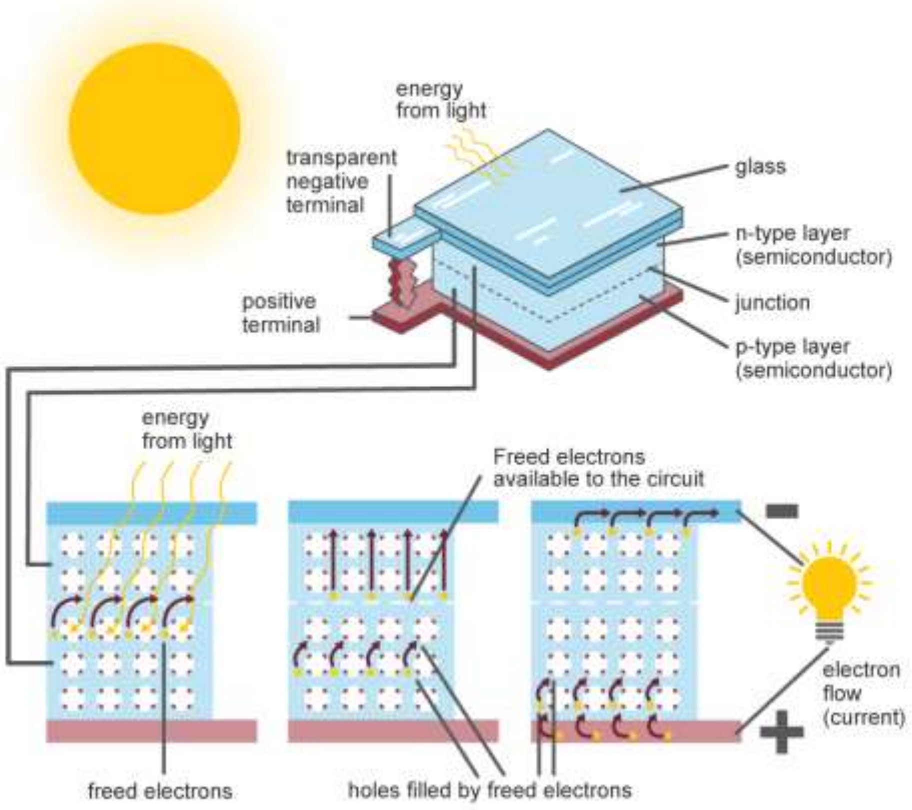




Photovoltaic Cells

- A solar cell is a device that converts the energy of sunlight directly into electricity by the photovoltaic effect.
- The photovoltaic effect involves creation of a voltage (or a corresponding electric current) in a material upon exposure to electro-magnetic radiation.
- Though the photovoltaic effect is directly related to the photoelectric effect, the two processes are different.
- There are several different types of PV cells which all use semiconductors to interact with incoming photons from the Sun in order to generate an electric current.
- Highly purified silicon (Si) from sand, quartz, etc. is "doped" with intentional impurities at controlled concentrations often used in Photovoltaic Cells.

Photovoltaic Mechanism



Source: U.S. Energy Information Administration

Solar Energy Conversion - Why Silicon?

- Silicon is the **2nd most abundant element (~ 28 % by mass) after oxygen (46 % by mass).**
- Highly pure Si can be synthesized from sand by heating at high temperature in furnace.

$$SiO_2 + C \rightarrow Si + CO_2$$

- **Si is an excellent semiconductor** with optimum band gap of **1.23 eV at 300 K.**
- **Cost effectiveness and can be easily doped with P, As, Sb, B, In or Al**.

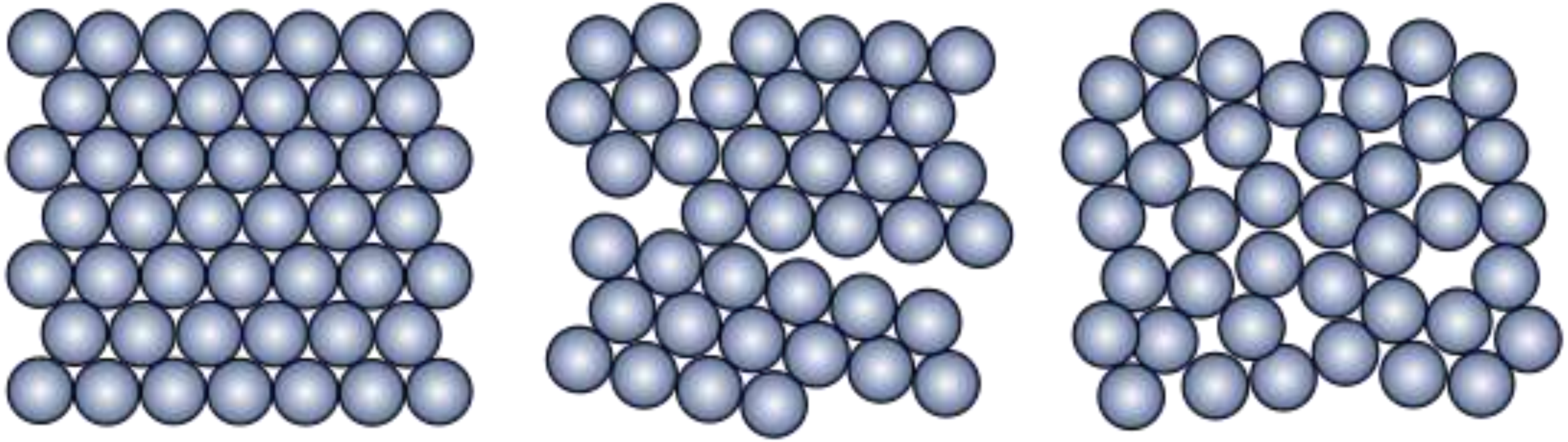
Types of Photovoltaics (PV) based on Si crystal structure and atomic arrangement:

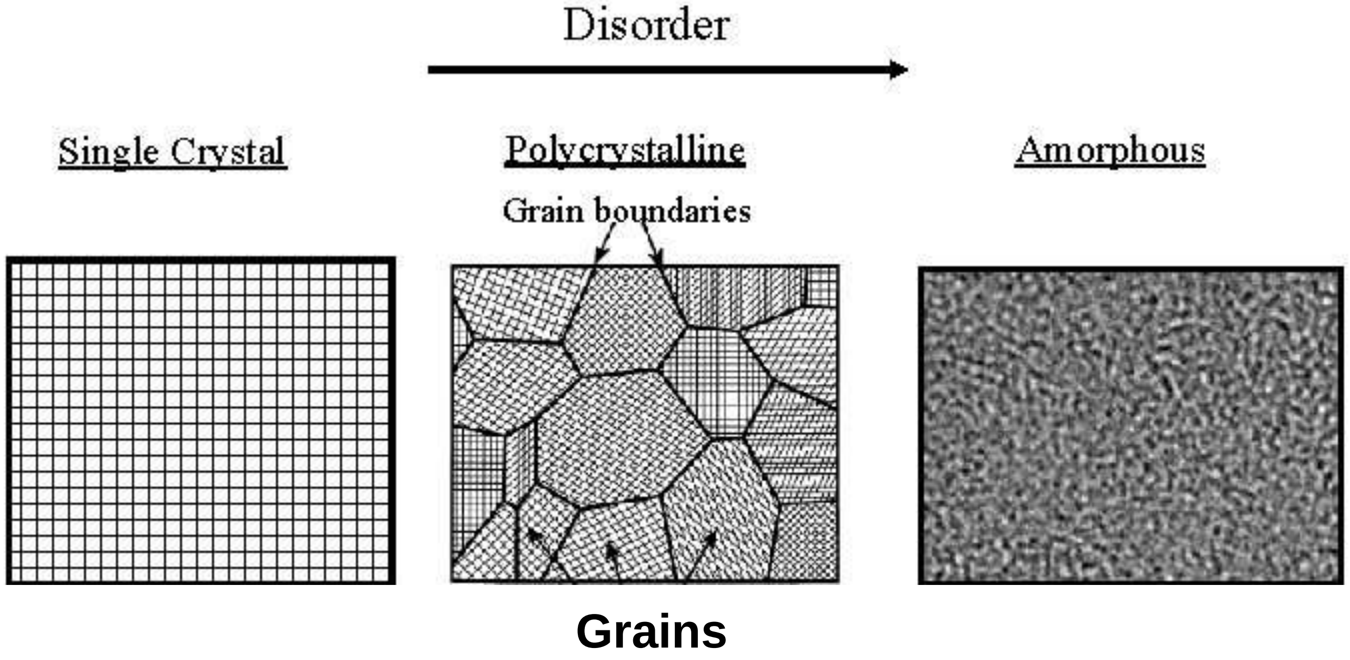
Single-crystal silicon	Poly-crystalline silicon	Amorphous silicon
Composed of an ordered array of component atoms. *This array is repetitive with displacement through the sample.*	Composed of a number of independently oriented crystalline sub-sections. *At their interfaces, the atomic order and regularity undergo sharp discontinuities.*	*Composed of irregular arrangement of atoms on any macroscopic scale; Non-crystalline.*
15–18% efficiency	12–16 % efficiency	4–8 % efficient
Expensive to make; grown as big crystal.	Cheaper to make; cast as ingots.	Cheapest to make per Watt; forms thin film.

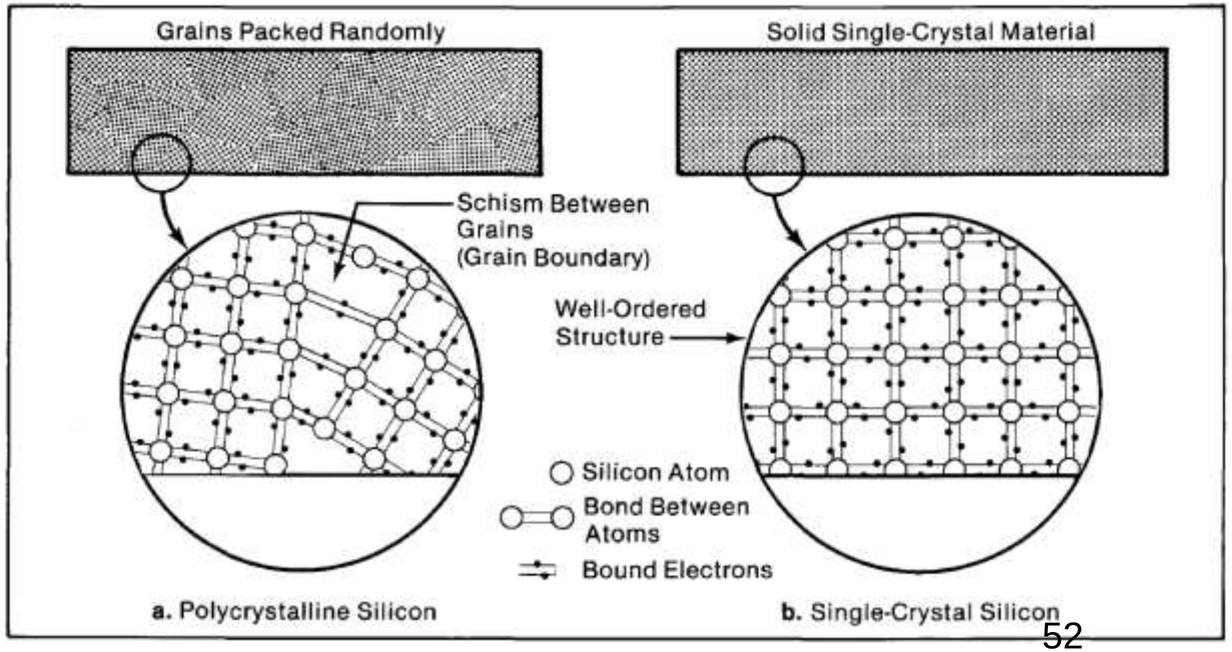
Electrode Conditions for Efficient Solar Energy Conversion

- **Band gap (E_g) should be optimum.**
- **Doping level should be optimum**, so that there will be a good spatial separation of the photo-generated carriers, and hence high quantum efficiency.
- **Should have large values of absorption co-efficient (α).**

(a). Single-crystal silicon:	**(b). Poly-crystalline silicon:**	**(c). Amorphous silicon**

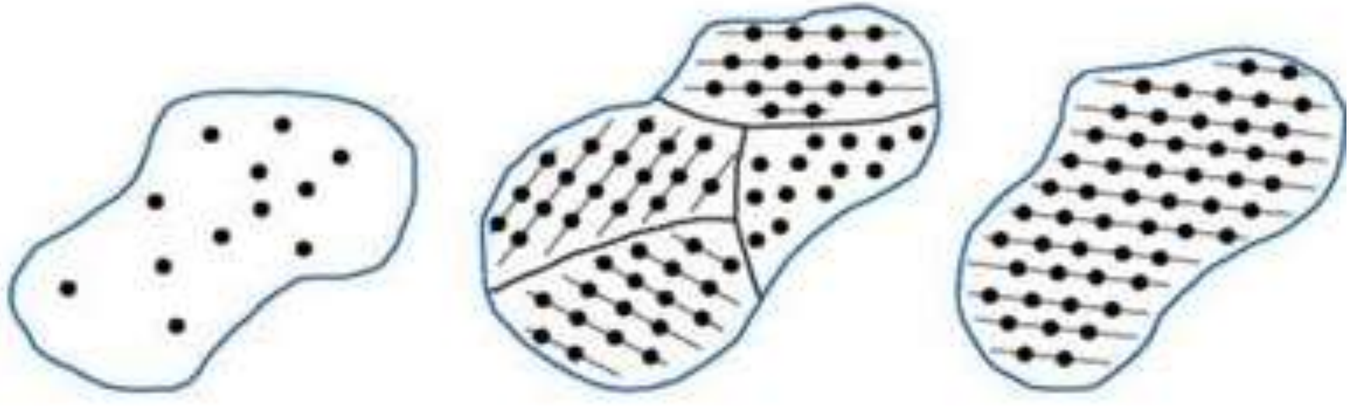




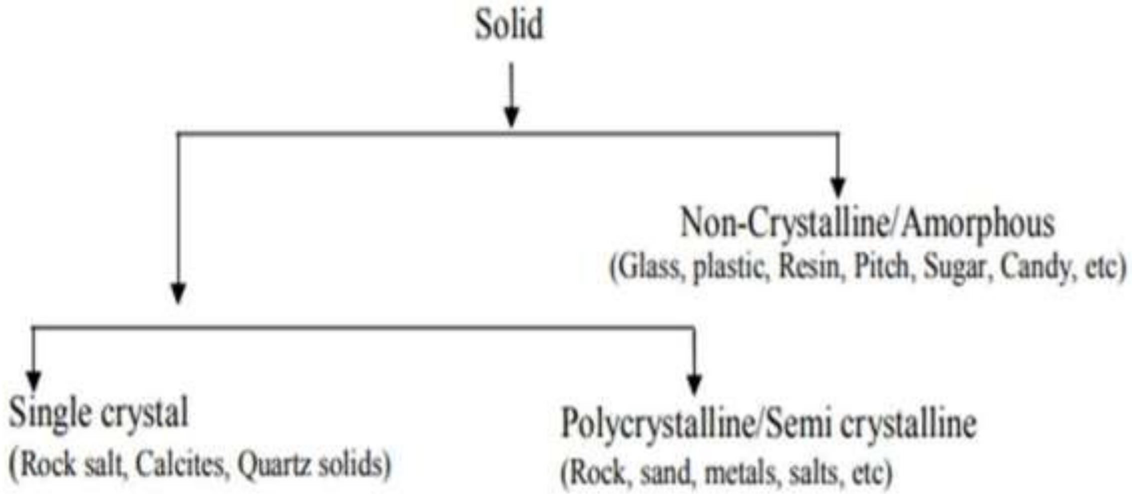


Three general types of solids

1. Amorphous — with order only within a few atomic and molecular dimensions (Fig. (a))
2. Polycrystalline — with multiple single-crystal regions (called grains) separated by grain boundary (Fig.(b))
3. Single crystal — with geometric periodicity throughout the entire material (Fig. (c))



(a) (b) (c)

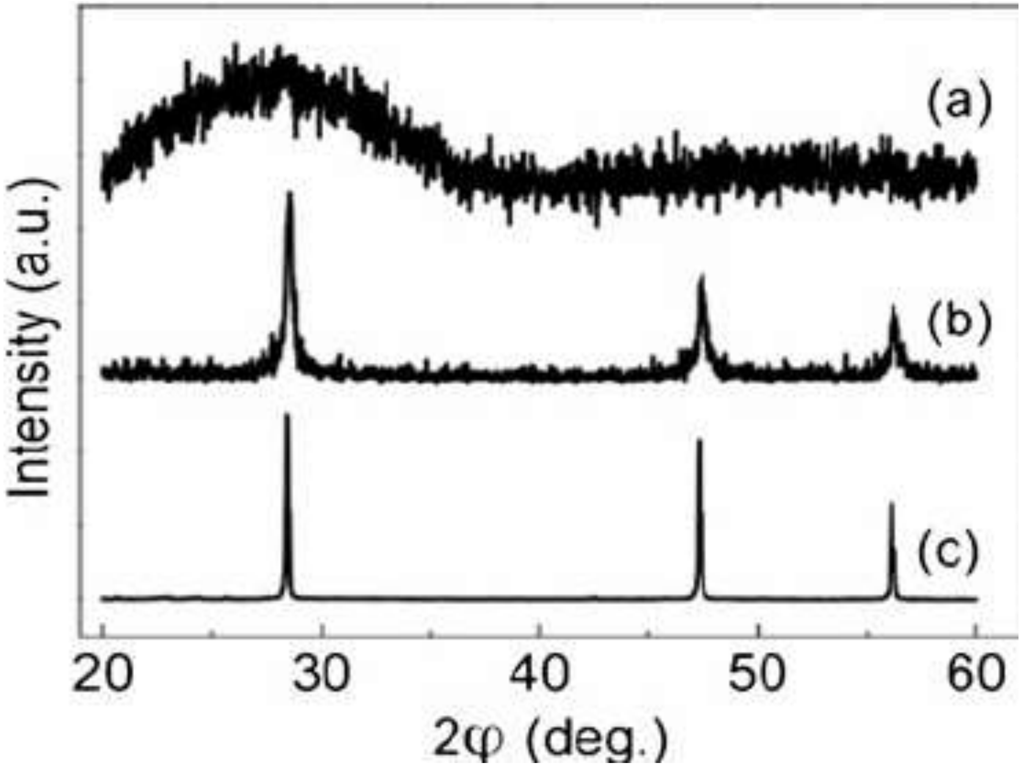


Solid

Non-Crystalline/Amorphous
(Glass, plastic, Resin, Pitch, Sugar, Candy, etc)

Single crystal
(Rock salt, Calcites, Quartz solids)

Polycrystalline/Semi crystalline
(Rock, sand, metals, salts, etc)

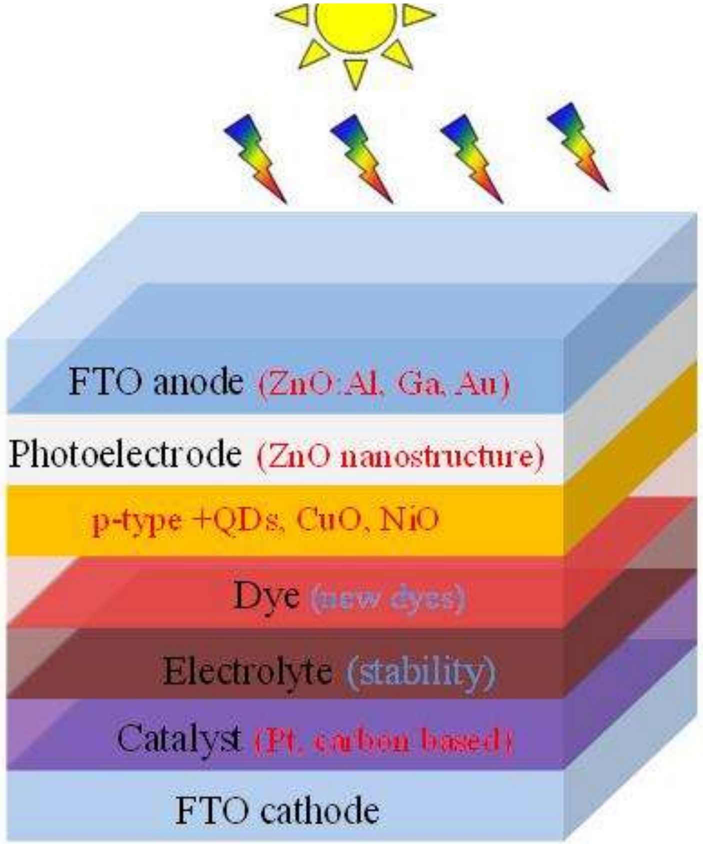


Dye-Sensitized Solar Cell (DSSC):

Components of DSSC

1).Transparent and Conducting Anode

- Substrate for the deposition of the semiconductor and catalyst, also acting as current collectors.
- Indium-doped tin oxide (ITO) films as conductive layer have > 80% transmittance and 18 Ω /cm^2 of sheet resistance.
- Fluorine-doped tin oxide (FTO) films as conductive layer show ~75% transmittance and 8.5 Ω /cm^2 of sheet resistance.



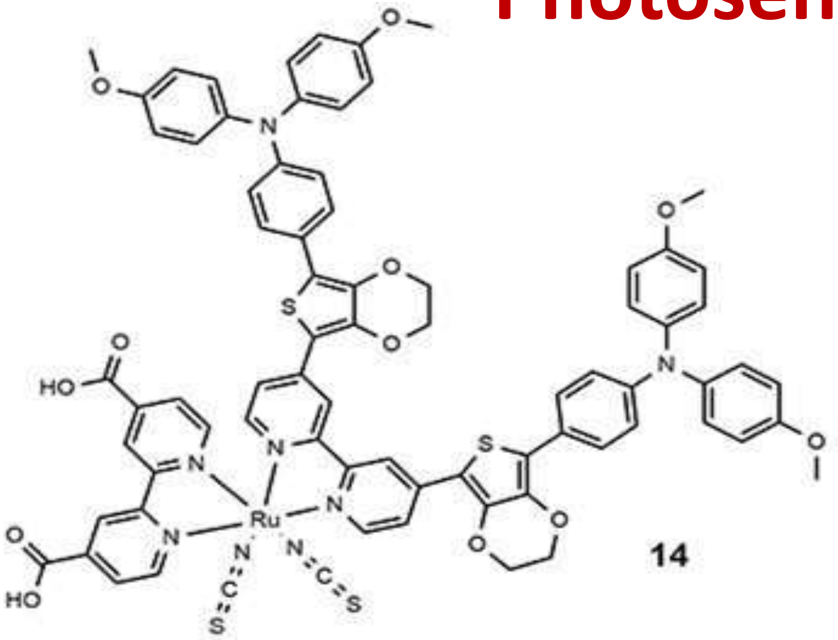
2. Working Electrode (WE)

- WE are prepared by depositing a thin layer of oxide semiconducting materials such as **TiO_2**, Nb_2O_5, **ZnO**, SnO_2 (**n-type**) and NiO (**p-type**) on the transparent/conducting FTO or ITO glass plate.
- These oxides have a wide energy band gap of 3~3.2 eV.
- Due to its **non-toxicity, and easy availability, TiO_2 is mostly used as a semiconducting layer**.
- To enhance its activity, TiO_2 semiconducting layers are immersed in a mixture of a photosensitive molecular sensitizer and a solvent.
- Due to highly porous structure and the large surface area of the electrode, a high number of dye molecules get attached on the nanocrystalline TiO_2 surface, and thus, light absorption at the semiconductor surface increases.

3. Photosensitizer - Dye

- Dye are responsible for the maximum absorption of light.
- Should be luminescent.
- Their absorption spectra should cover UV-vis and NIR regions.
- Periphery of the dye should be hydrophobic to enhance long-term stability of cells.
- Co-absorbents like chenodeoxycholic acid or anchoring groups like alkoxy-silyl, phosphoric acid and -COOH should be present to avoid aggregation of dye over TiO_2 surface.

Photosensitizer or Dye



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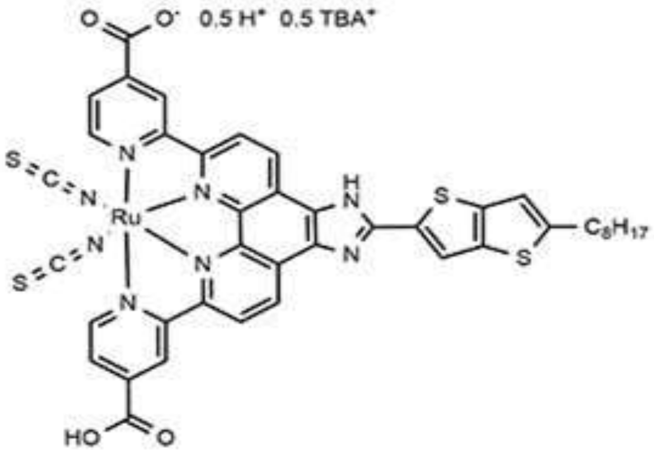

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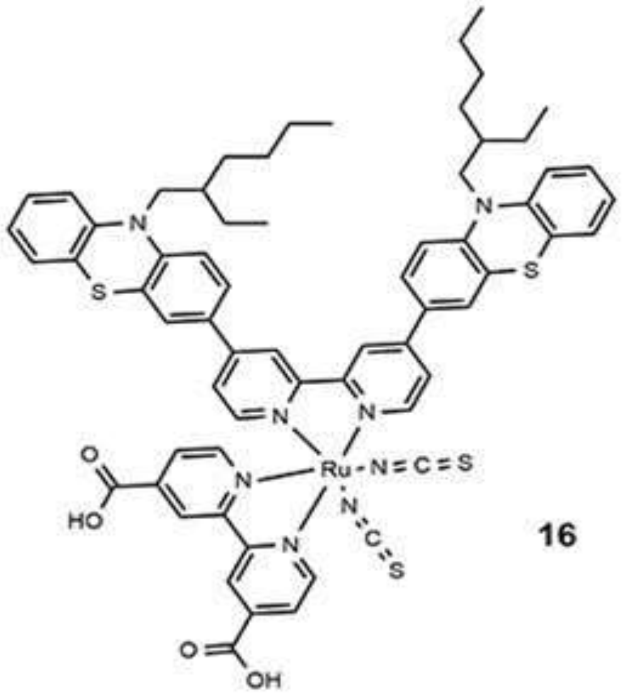

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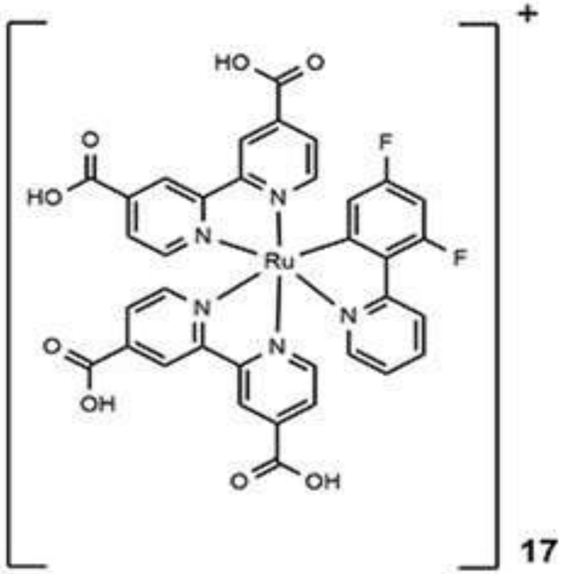

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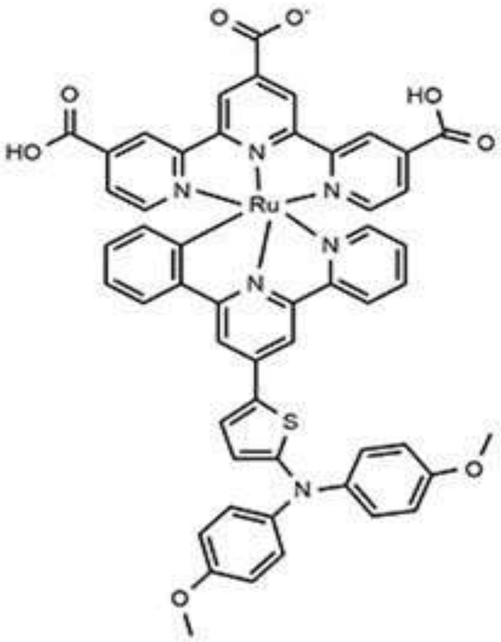

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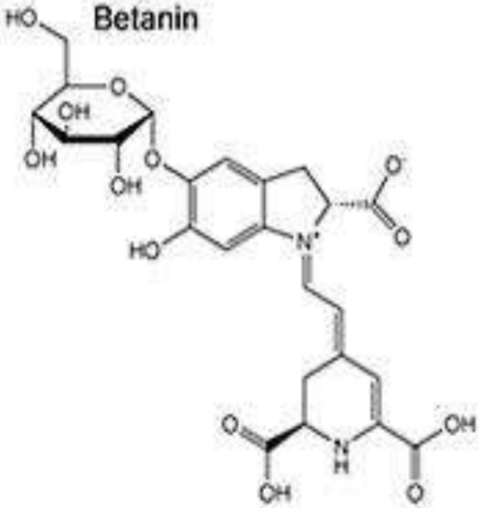
Naturally Occurring Dyes

Beetroot (Beta vulgaris)

Grapes skin (Vitis vinifera)

Raspberry (Rubus idaeus)

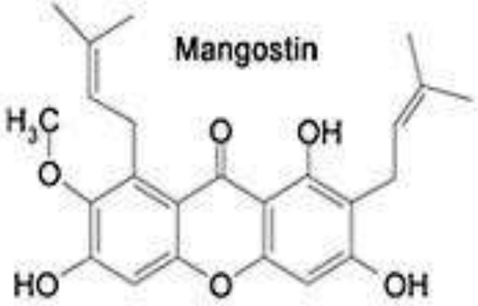
Betanin



Cyanidin

Pelargonidin

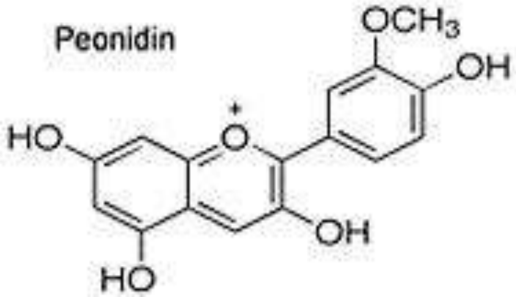
Mangostin



Black plum (Syzygium cumini)

Mangostee (Garcinia Mangostanan)

Peonidin



4. Electrolyte

- I^-/I_3^-, Br^-/Br_2^-, SCN^-/SCN_2 and Co(II)/Co(III) used as electrolyte.
- Electrolyte has five main components: redox couple, solvent, additives, ionic liquids and cations.

Requisite properties of the electrolyte:

  - Redox couple should be able to regenerate the oxidized dye efficiently.
  - Should have chemical, thermal and electrochemical stability.
  - Should be non-corrosive with DSSC components.
  - Should be able to permit fast diffusion of charge carriers.
  - Enhance conductivity and
  - Create effective contact between the working and counter electrodes.

5. Counter Electrode (CE)

- **CE in DSSCs are mostly prepared by using Pt, C, CoS, Au/GNP, alloy CEs like FeSe, and $CoNi_{0.25}$.**

The Grätzel Cell

Grätzel cell prepared from *Hibiscus tea*.

Upper Plate: Dye coated TiO_2 Plate (-ve)

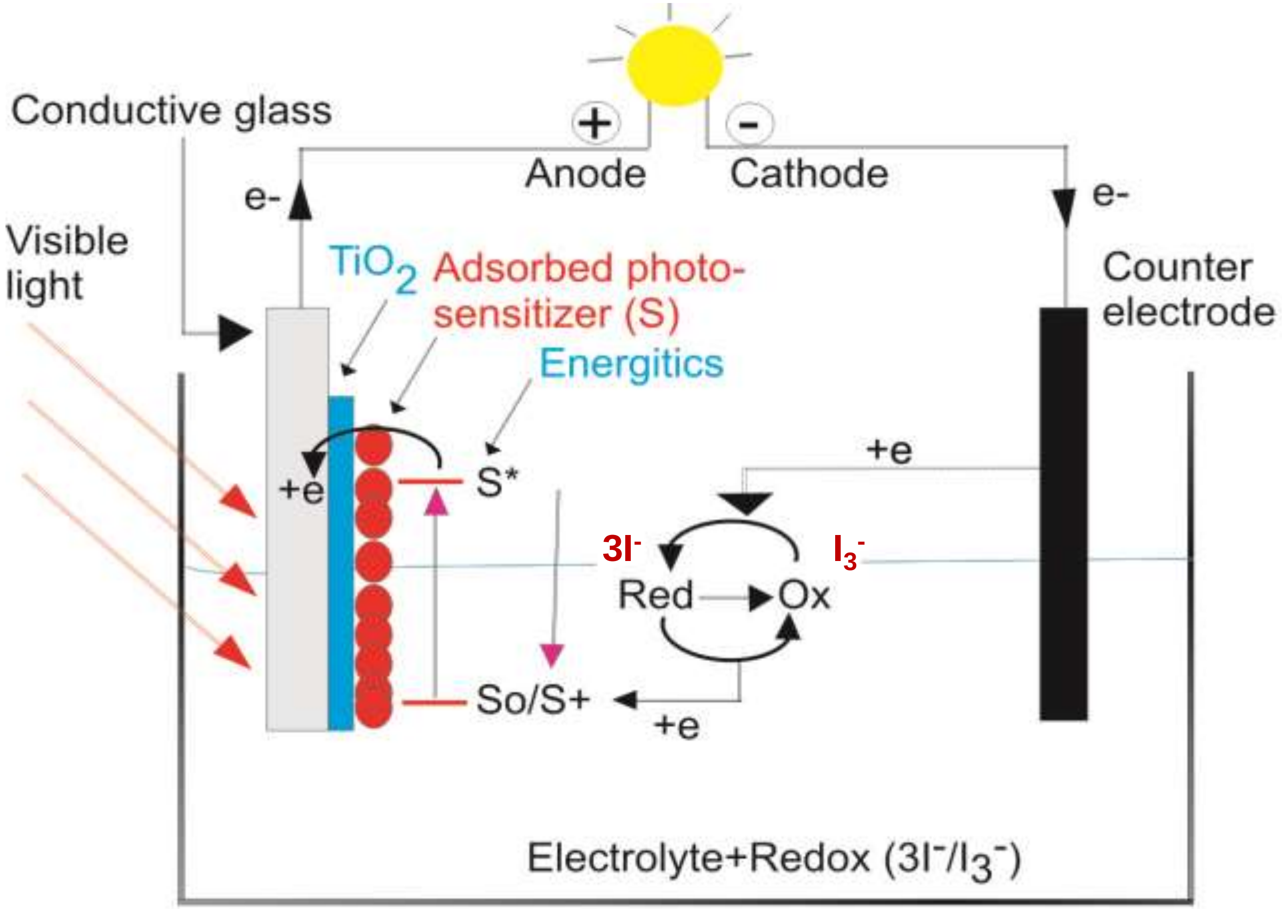
Lower Plate: Graphite coated conductor (+ve)

- In Grätzel cell a range of organic dyes are used.

  Eg. Ruthenium- Polypyridine, Indoline dye & metal free organic dyes.
- These dyes are extractable from simple foods such as *Hibiscus tea, tinned summer fruits, blackberries*.

Construction:

- Two transparent glass plates were taken and their inner sides are coated with a transparent thin layer of a conducting material.
- Onto the conducting sides, 1st glass plate is coated with titanium dioxide (TiO_2). and the 2nd glass plate is coated with graphite.
- A dye is then adsorbed onto the TiO_2 layer by immersing the plate into a dye solution of 0.1 mM in alcohol for 10 min.(approx.)
- The plates are then carefully sandwiched together and secured using a paperclip.
- To complete the cell, a drop of iodide electrolyte is added between the plates.
- The upper plate is the TiO_2 plate, dyed with *Hibiscus tea* and the lower plate is coated with graphite.



$$TiO_2|S + h\nu \rightarrow TiO_2|S^* \qquad (1)$$

$$TiO_2|S^* \rightarrow TiO_2|S^+ + e_{cb} \qquad (2)$$

$$TiO_2|S^+ + e_{cb} \rightarrow TiO_2|S \qquad (3)$$

$$TiO_2|S^+ + 3/2\ I^- \rightarrow TiO_2|S + 1/2\ I_3^- \qquad (4)$$

$$1/2\ I_3^- + e_{(Pt)} \rightarrow 3/2\ I^- \qquad (5)$$

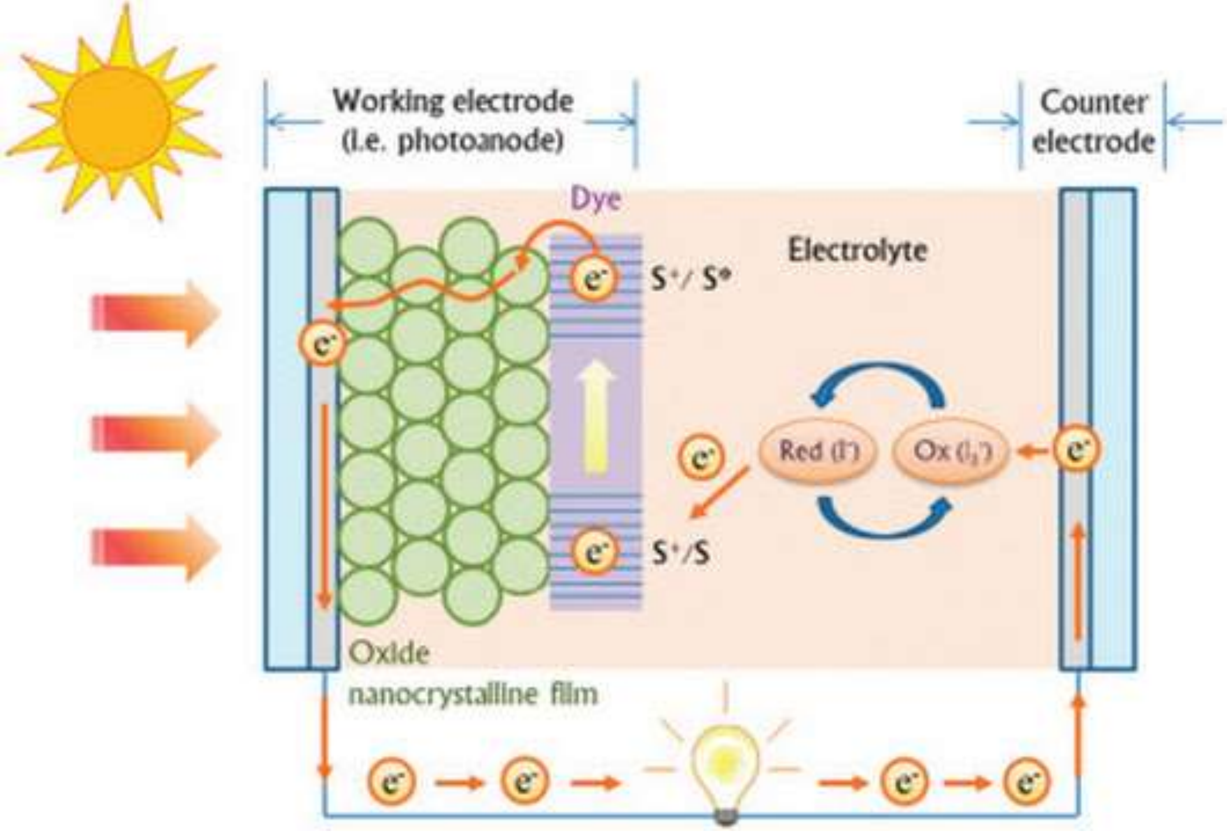
$$I_3^- + 2\ e_{cb} \rightarrow 3\ I^- \qquad (6)$$

Photo-sensitizer (S) = $Ru(bpy)_3^{2+}$; bpy = bipyridyl legand

So = ground state (reduced); S+ = oxidized; S* excited state

Working Principle of Grätzel Cell

- Sunlight energy passes through TiO_2 layer and strikes the adsorbed dye molecules.
- Electrons gain this energy and become excited. The excited electrons escape from the dye molecules to become free electrons.
- These free electrons move through the TiO_2 and accumulate at the –ve plate (dyed TiO_2 plate).
- The free electrons then start to flow through the external circuit to produce an electric current. This electric current powers the light bulb.



- To complete the circuit, the dye is regenerated by the following process: The dye regains its lost electrons from the iodide electrolyte.
- Iodide (I^-) ions are oxidised to tri-iodide (I_3^-). The free electrons at the graphite plate then reduce the tri-iodide molecules back to their iodide state.
- The dye molecules are then ready for the next *excitation/oxidation/reduction* cycle.

Advantages and disadvantages of DSSC

Advantages

- Ability to Work at Wider Angles and in Low Light
- Long Life
- Good Price/Performance Ratio
- Low Cost
- Mechanical Robustness
- Ability to Operate at Lower Internal Temperatures
- Lowering the electricity bills

Disadvantages

- DSSC design is the use of the liquid electrolyte
- which has temperature stability problems
- costly ruthenium (dye), platinum(catalyst)
- the electrolyte solution contains volatile organic compounds (or VOC's),