Engineering Chemistry (BCHY101L)

Module 4

Energy Devices

Contents…. (6 hours)

- Electrochemical and electrolytic cells
- Electrode materials with examples
  - Semi-conductors
- Chemistry of Li ion secondary batteries
- Supercapacitors
- Fuel cells: H_2-O_2 and solid oxide fuel cell (SOFC)
- Solar cells: Photovoltaic cells (silicon based), Photoelectrochemical cells, Dye- sensitized cells.

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. $\Delta G > 0$

Galvanic or voltaic cell

- A galvanic cell uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to generate electricity.
- This type of electrochemical cell is also called a voltaic cell after its inventor, the Italian physicist Alessandro Volta.
- Anode is written on the left-hand side >> oxidation occurs
- Cathode is written on the right-hand side >> reduction occurs

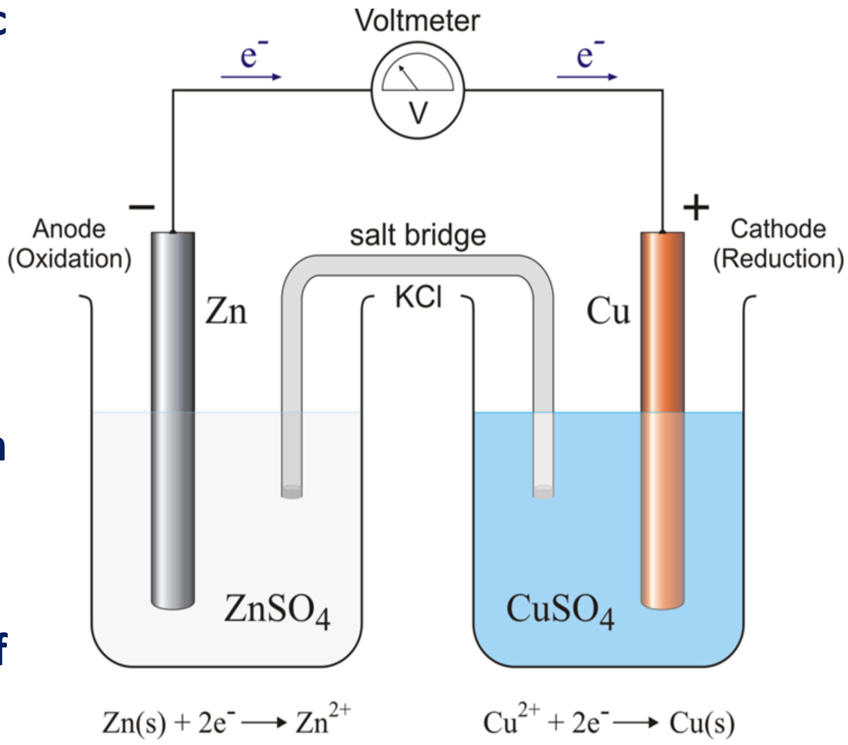
Electrode on the left	Electrode on the right
Metal (or solid phase)| Electrolyte (whole formula or ion)	Electrolyte (whole formula or ion) | Metal (or solid phase)
$Zn \| Zn(NO_3)_2$ (1M)	$Cu(NO_3)_2$ (1M) $\| Cu$
Oxidation: $M_1 \rightarrow M_1^{n+} + n\,e^-$	Reduction: $M_2^{n+} + n\,e^- \rightarrow M_2$

Overall representation of Galvanic cell

$$M_1 \mid M_1^{n+}\,(C_1) \parallel M_2^{n+}\,(C_2) \mid M_2$$

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
- Maintains the charge balance in the two half cells
- Minimizes or eliminates the liquid junction potential
- Cell emf = 1.1 V



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

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:**

$$\boxed{E_{cell} = E^0_{M_1} - E^0_{M_2} + \frac{0.059}{n}\log_{10}\frac{[M_1^{n+}]}{[M_2^{n+}]}}$$

$E^0_{M_1} = Standard\ reduction\ potential\ of\ cathode, M_1$

$E^0_{M_2} = Standard\ reduction\ potential\ of\ cathode, M_2$

- **For equimolar solution of electrolytes corresponding to M_1 and M_2:**

$$\boxed{E_{cell} = E^0_{M_1} - E^0_{M_2}}$$

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:** $Cd + Cu^{2+} \rightarrow Cu + Cd^{2+}$

- ***Cell EMF:***

$$E_{cell} = 0.34 - (-0.40) + \frac{0.059}{2}\log_{10}\frac{[0.5]}{[0.01]}$$

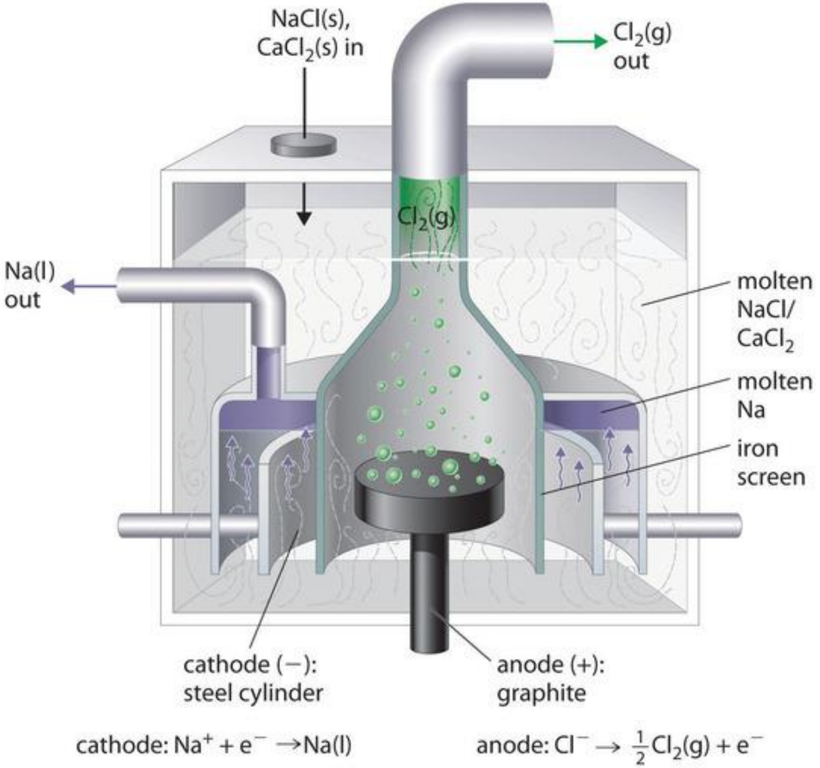
$$= 0.74 + \frac{0.059}{2}\log_{10} 50$$

$$= 0.74 + \frac{0.059}{2} \times 1.7$$

$$= 0.74 + 0.05 = 0.79\ V$$

The Electrolysis of Molten NaCl

- Here Na^+ ions gain electrons and are reduced to Na at the cathode.
- As Na^+ ions near the cathode are depleted, additional Na^+ ions migrate in.
- Similarly, there is net movement of Cl^- ions to the anode where they are oxidized to Cl_2.
- Positive terminal is connected to the anode.
- The negative terminal is connected to the cathode which forces electrons to move from the anode to the cathode.
- Electrolysis is performed at ~ 801 °C.
- Here inert electrodes are used.



Cathode: $2\,Na^+(l) + 2\,e^- \rightarrow 2\,Na\,(l)$

Anode: $2\,Cl^-(l) \rightarrow Cl_2\,(g) + 2\,e^-$

➡ Overall: $2\,NaCl\,(l) \rightarrow 2\,Na\,(l) + Cl_2\,(g)$

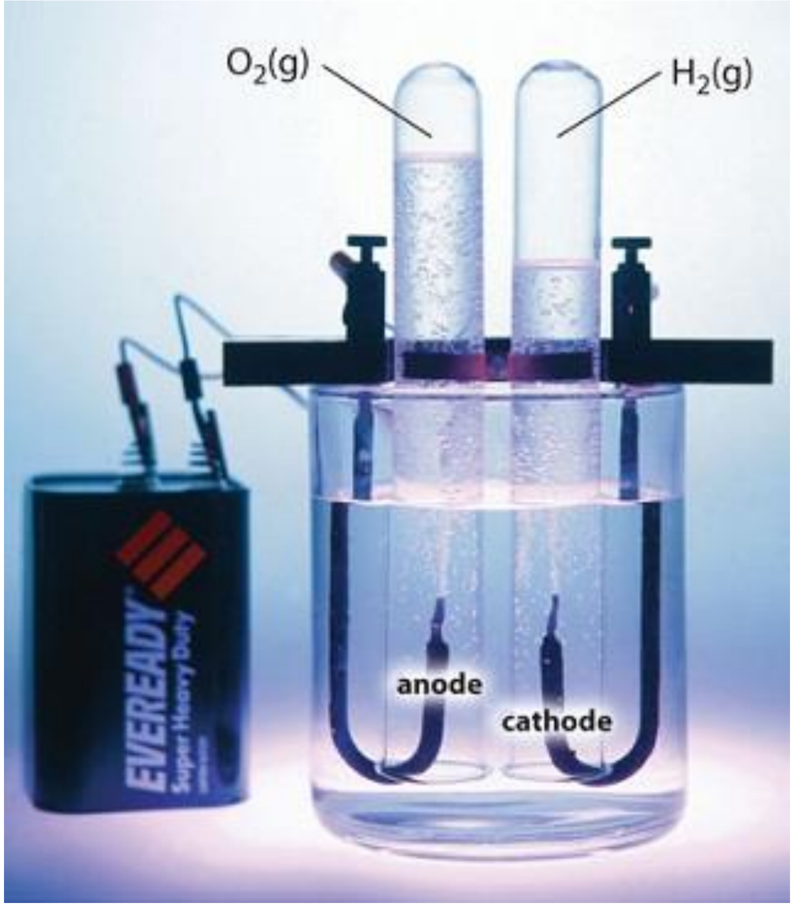
Electrolytic Decomposition of Water

- A pair of inert electrodes are dipped into the solution and applying a voltage between them results in the rapid evolution of bubbles of H_2 and O_2.
- Due to very poor electrical conductivity of pure water, a small amount of an ionic solute (such as k_2SO_4 or Na_2SO_4) is added to increase its electrical conductivity.
- The electrolytes are chosen such a way that the ions that are harder to oxidize or reduce than water:

Cathode: $4\ H^+(aq) + 4\ e- \rightarrow 2\ H_2(g)$

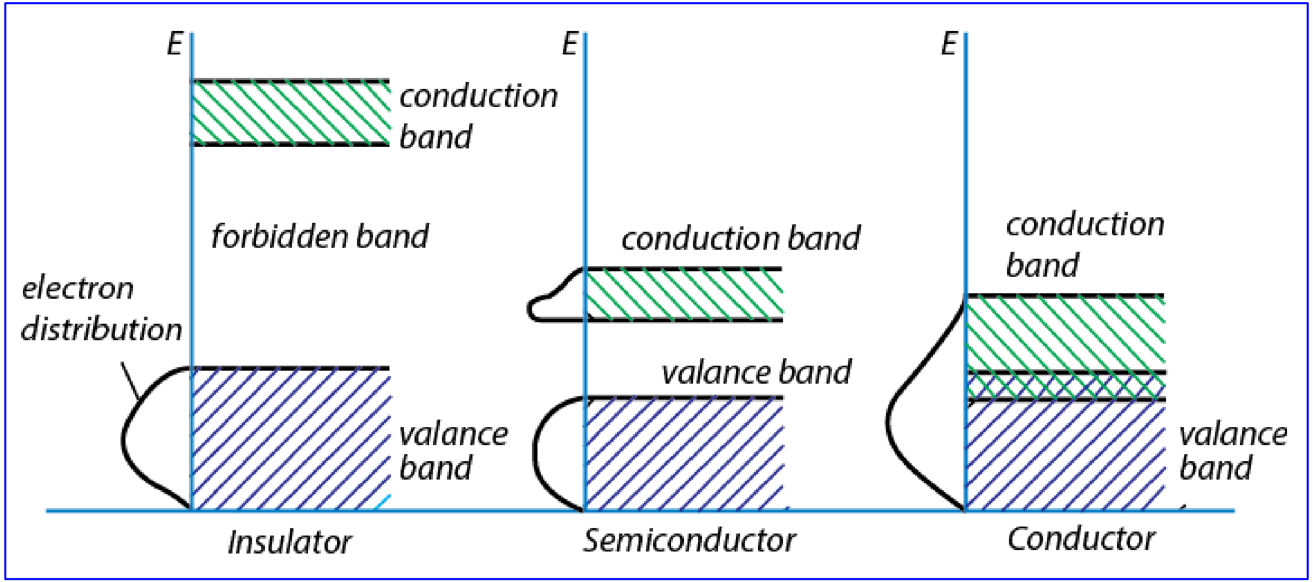
Anode: $2\ H_2O \rightarrow O_2(g) + 4\ H^+ + 4\ e^-$

Overall: $2\ H_2O \rightarrow O_2(g) + 2\ H_2(g)$



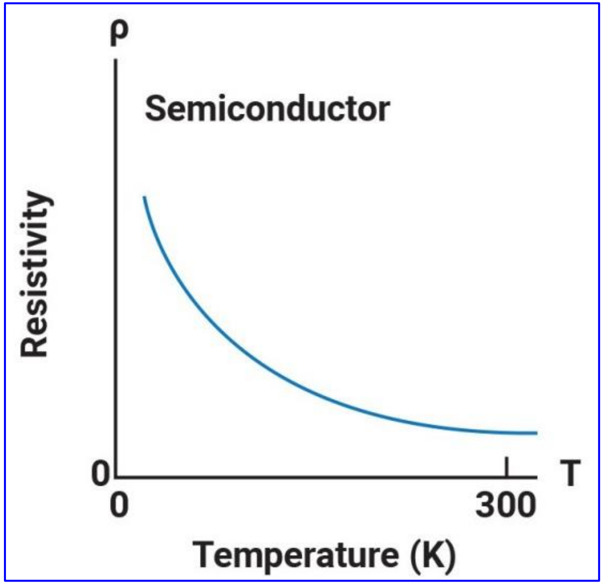
Semiconductors

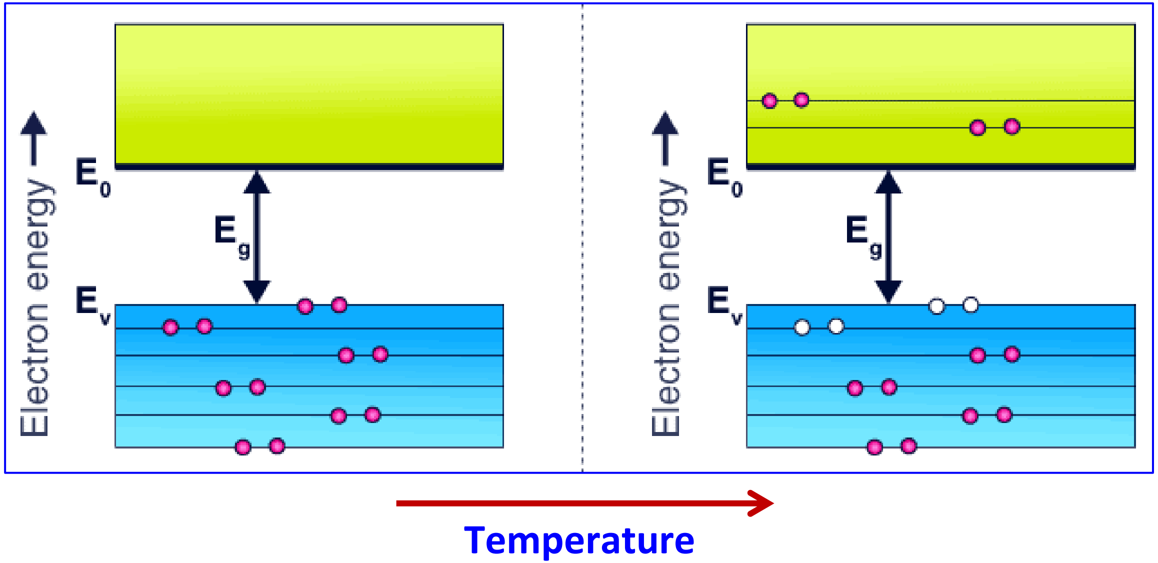
- A semiconductor is a substance, usually a solid chemical element or compound that can conduct electricity under some conditions but not others, making it a good medium for the control of electrical current.
- It has almost filled valence band, empty conduction band and very narrow energy gap i.e., of the order of 1 eV. Energy gap of Silicon (Si) and Germanium (Ge) are 1.0 and 0.7 eV respectively. Consequently Si and Ge are semiconductors.



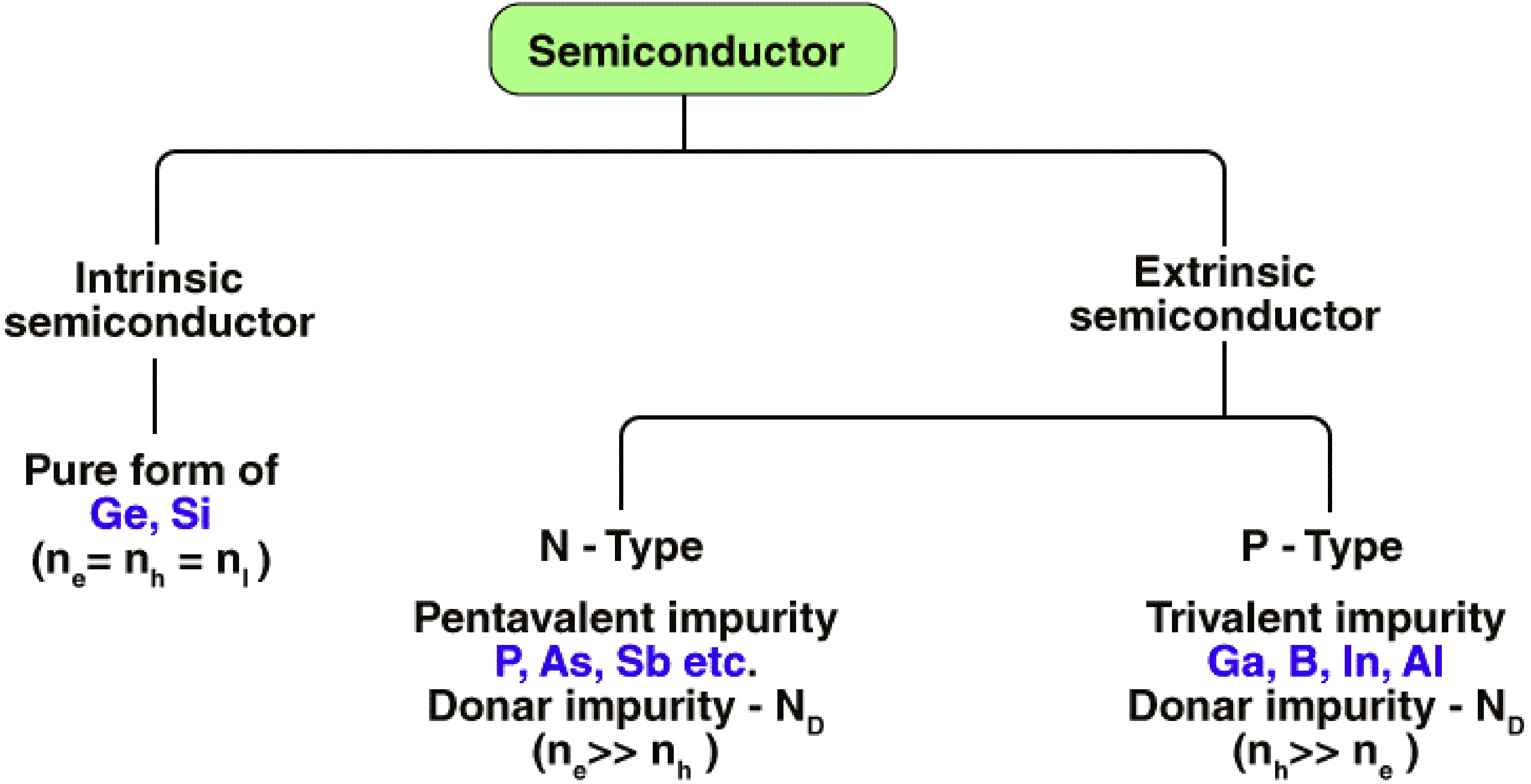
Effect of temperature on conductivity of semiconductors:

- At 0 K electrons freeze at valence band and hence all semiconductors are insulators.
- Electrical conductivity of a semiconductor material increases with increasing temperature as resistivity decreases.
- At higher temperature transition from the valence band to the conduction band gets facilitated $\Rightarrow$ higher conductivity or lower resistivity.





Types of semiconductors:

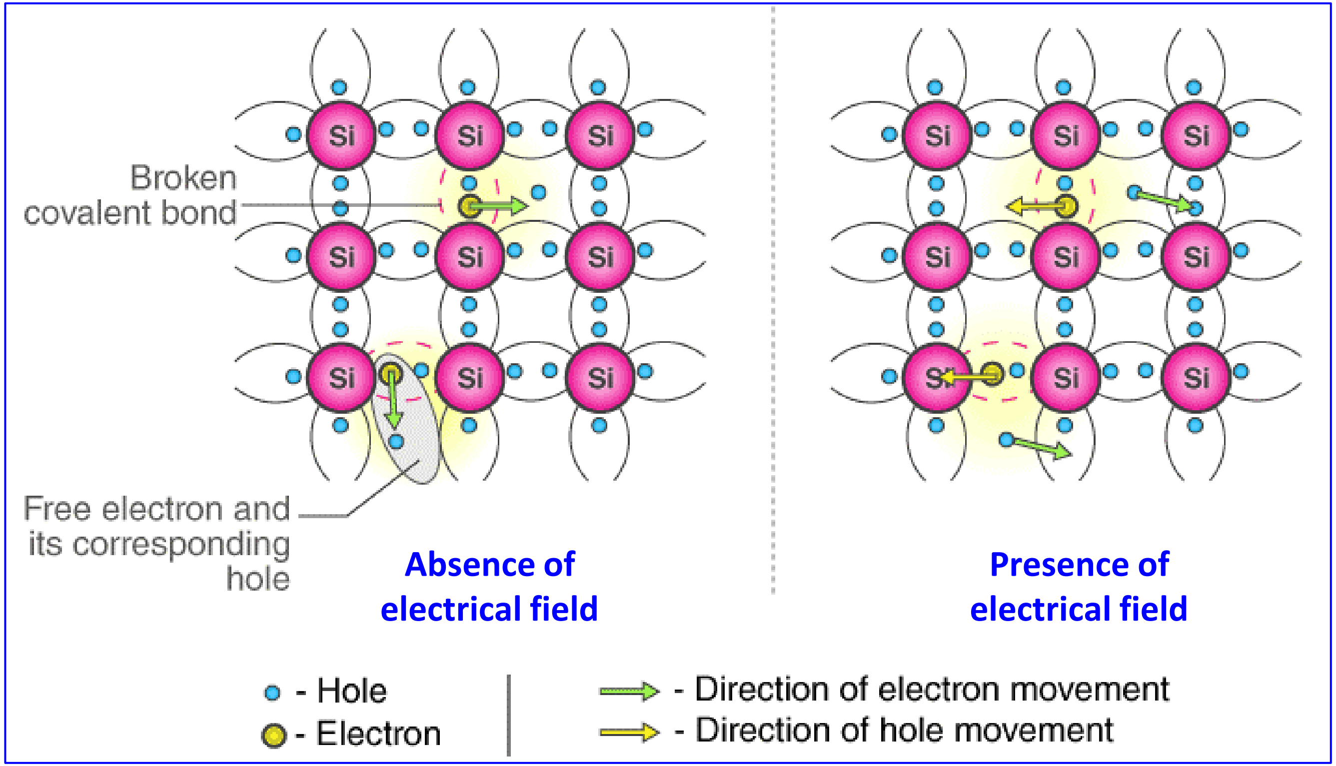


Semiconductor

- Intrinsic semiconductor
  - Pure form of **Ge, Si** ($n_e = n_h = n_i$)
- Extrinsic semiconductor
  - N - Type
    - Pentavalent impurity
    - **P, As, Sb etc.**
    - Donar impurity - N_D
    - ($n_e >> n_h$)
  - P - Type
    - Trivalent impurity
    - **Ga, B, In, Al**
    - Donar impurity - N_D
    - ($n_h >> n_e$)

Intrinsic Semiconductor

- **Intrinsic semiconductor material is chemically very pure and possesses poor conductivity.**
- **It has equal numbers of negative carriers (electrons) and positive carriers (holes)**

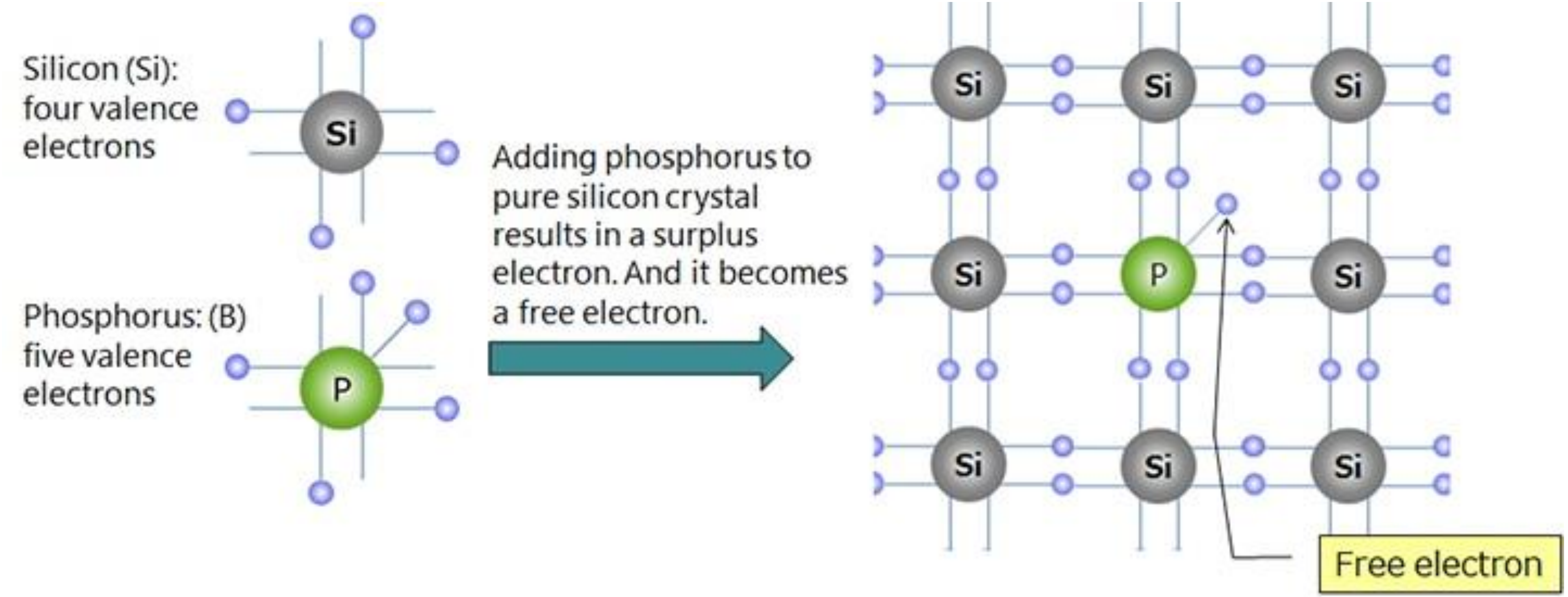


Extrinsic Semiconductor.

- 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.
- Introducing impurities into the semiconductor materials (doping process) can control their conductivity.
- Doping process produces two groups of semiconductors:
  - The negative charge conductor (*n*-type)
  - the positive charge conductor (*p*-type)
- Semiconductors are available as either elements or compounds.
- Silicon and Germanium are the most common elemental semiconductors.
- Compound Semiconductors include InSb, InAs, GaP, GaSb, GaAs, SiC, and GaN.

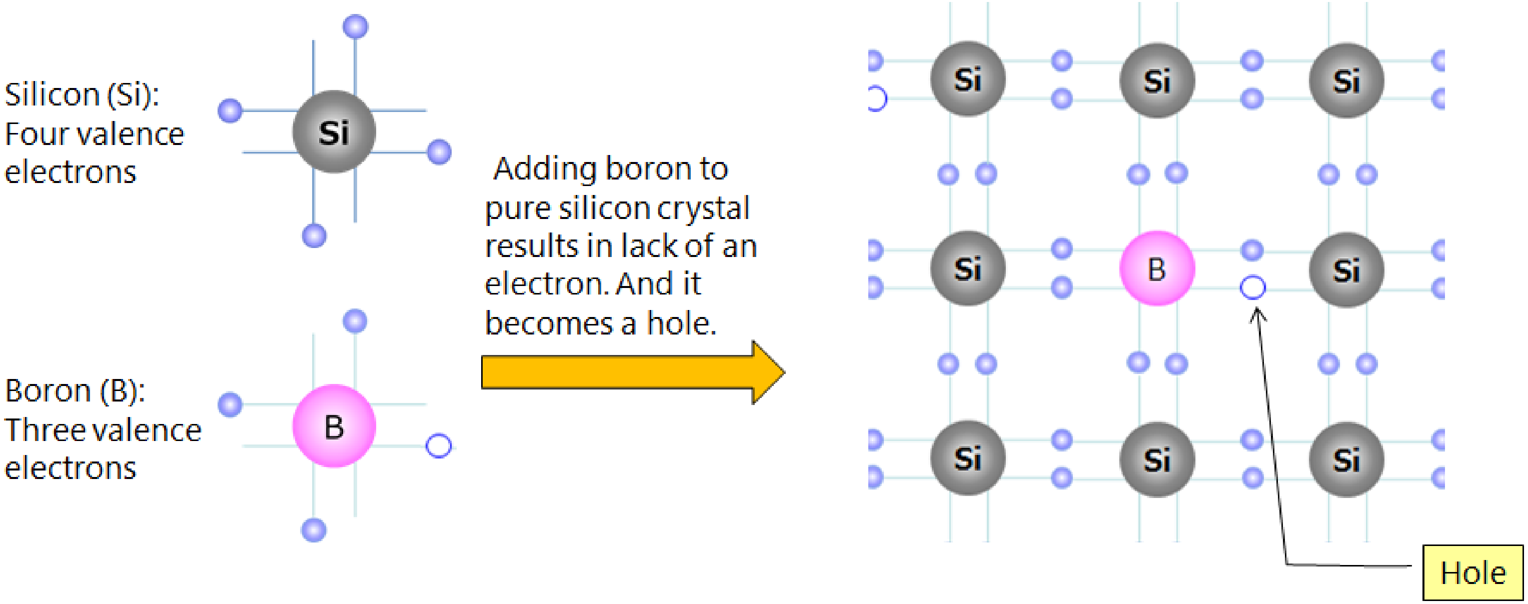
n-type Semiconductor

- 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 a pure silicon crystal, one of the valence electrons of phosphorus becomes free to move around (free electron) as a surplus 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 doped to a single crystal of silicon, valence electrons will be insufficient at one position to bond silicon and boron, resulting in holes that lack electrons.



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

Preparation of Semiconductors: ~ 99.9999% pure Si and Ge

- **Distillation:**
  - Separation of materials is based on the difference in boiling points.
  - For Ge ⇒ $GeCl_4$ and for Si ⇒ $SiHCl_3$
  - As is removed from $GeCl_4$ (b.p. 83.1 0 C) with the help of HCl.
  - Pure $GeCl_4$ is obtained by fractional distillation in presence of chlorine.
  - After cooling, the pure $GeCl_4$ is treated with extra pure water to get germanium oxide.
  - Subsequent reduction of $GeCl_4$ with pure hydrogen affords highly pure elemental Ge.

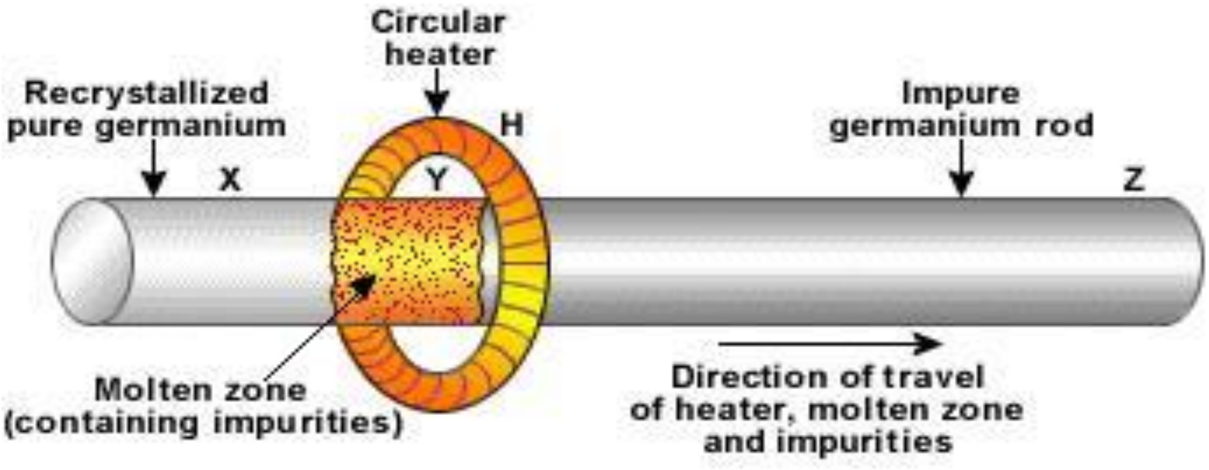
$$GeCl_4 \quad + \quad 2\,H_2O \quad \rightarrow \quad GeO_2 \quad + \quad 4\,HCl$$

$$GeO_2 \quad + \quad 2\,H_2 \quad \rightarrow \quad Ge \quad + \quad 2\,H_2O$$

  - Similarly, distilled trichloro silane ($SiHCl_3$) is employed to get silicon of high purity.

Zone refining

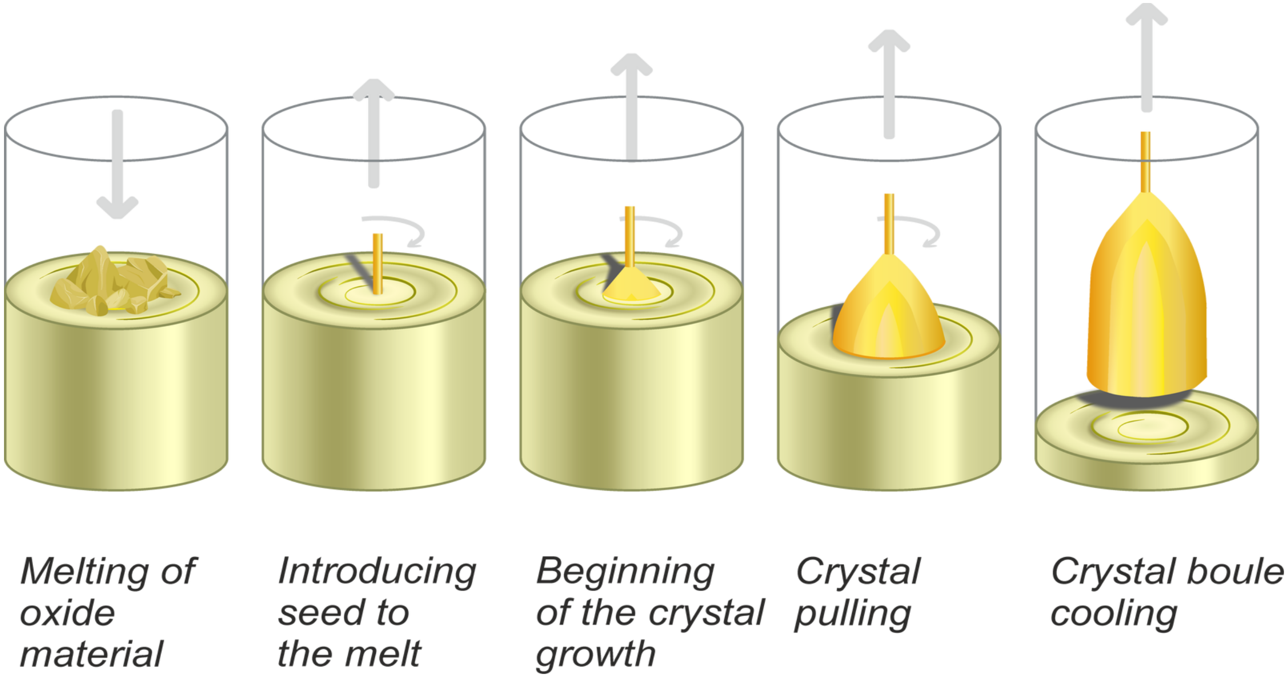
- Difference between solubility of impurities in the molten and solid phases is used to concentrate impurities at the end section of the ingots.
- The technique is based on the principle that when an impure metal in a molten state is allowed to cool, only the metal crystallizes while the impurities remain present in the molten state (mass) or melt.
- Used for the purification of germanium, silicon, gallium etc.

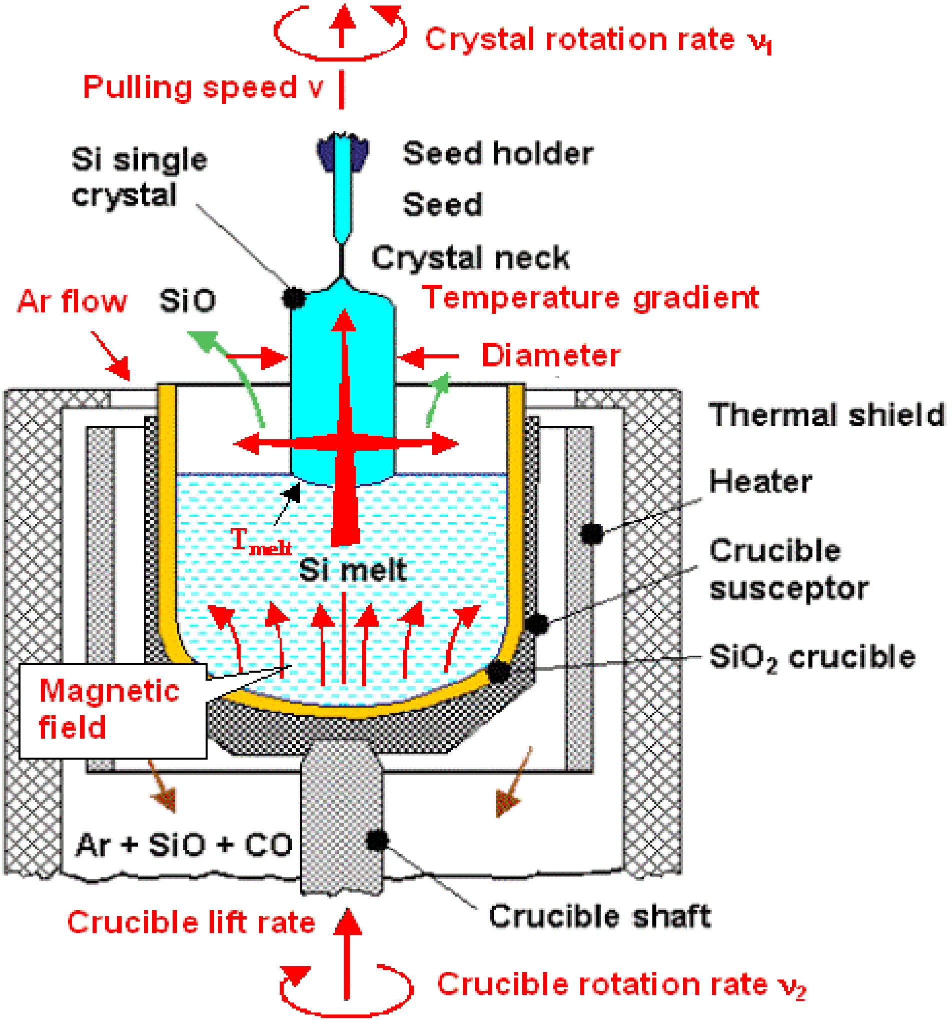


Zone refining of germanium metal.

Czochralski crystal pulling technique

- Ge or Si obtained by zone refining method is polycrystalline, i.e., there is no regularity in their crystal structure and contain crystals of different sizes.
- This method involves growing the crystal on a single crystal seed; thereby the atoms reproduce identical atomic arrangement as that of the seed crystal.





Silicon crystal with a diameter of 300 mm and a weight exceeding 250 kg

Doping techniques

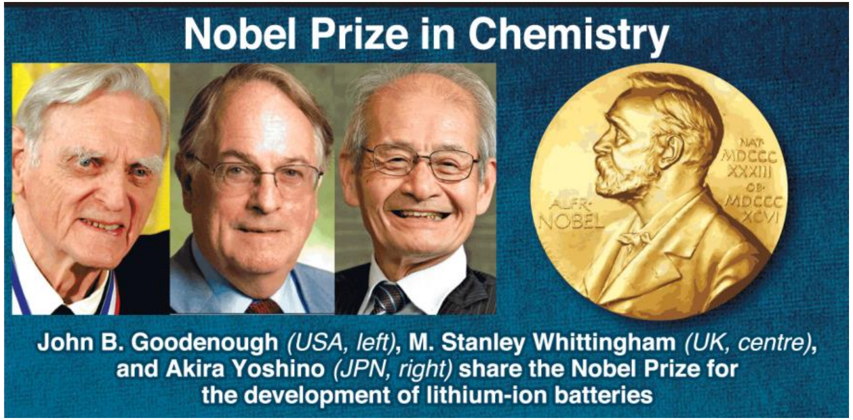
- **Epitaxy:**
  - Involves in unified crystal growth or deposition of a thin crystal on another substrate.
  - Si or Ge wafer (kept in graphite boat) is placed in a long cylindrical quartz tube reactor, which is then heated (by RF induction coil). Then gases containing compounds of Ge or Si mixed with calculated/appropriate quantities of dopant over the wafer results.
  - For getting Si epitaxial film, $SiCl_4$, H_2 and N_2 mixture is used.
  - For n-type doping $\Rightarrow$ above mixture is used with phosphine (PH_3)
  - For p-type doping $\Rightarrow$ Diborane (B_2H_6) is employed.
- **Diffusion technique:**
  - Conversion of a region of semiconductor material by solid or gaseous diffusion of impurity atom 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 even less than a few millions of a centimetre.

Battery

- Battery is a device that consists of one or more electrochemical cells connected in series or parallel or both and converts the chemical energy into electrical energy.
- The cell consists of three major components:
  - The anode: **Reducing electrode** which gives up electrons to the external circuit
  - The cathode: **Oxidizing electrode** which accepts electrons from the external circuit
  - The electrolyte: It is the **ionic conductor**
- **Types of Cells/Batteries:**
  - **Primary battery (Primary cells):** The cell reaction is not reversible. When all the reactants have been converted to product, no more electricity is produced, and the battery is dead. Example: Lechlanche Cell (Dry Cell), Alkaline Cell and Lithium batteries.
  - **Secondary battery (secondary cells):** The cell reactions can be reversed by passing electric current in the opposite direction. Example: Lead acid batteries, Ni-Cd batteries, Ni-Metal Hydride batteries, Lithium ion batteries.
  - **Flow battery and fuel cell:** Materials (reactants, products, electrolytes) pass through the battery. Example: Hydrogen-oxygen fuel cell (HOFC), Solid oxide fuel cell(SOFC), etc.

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.


Nobel Prize in Chemistry

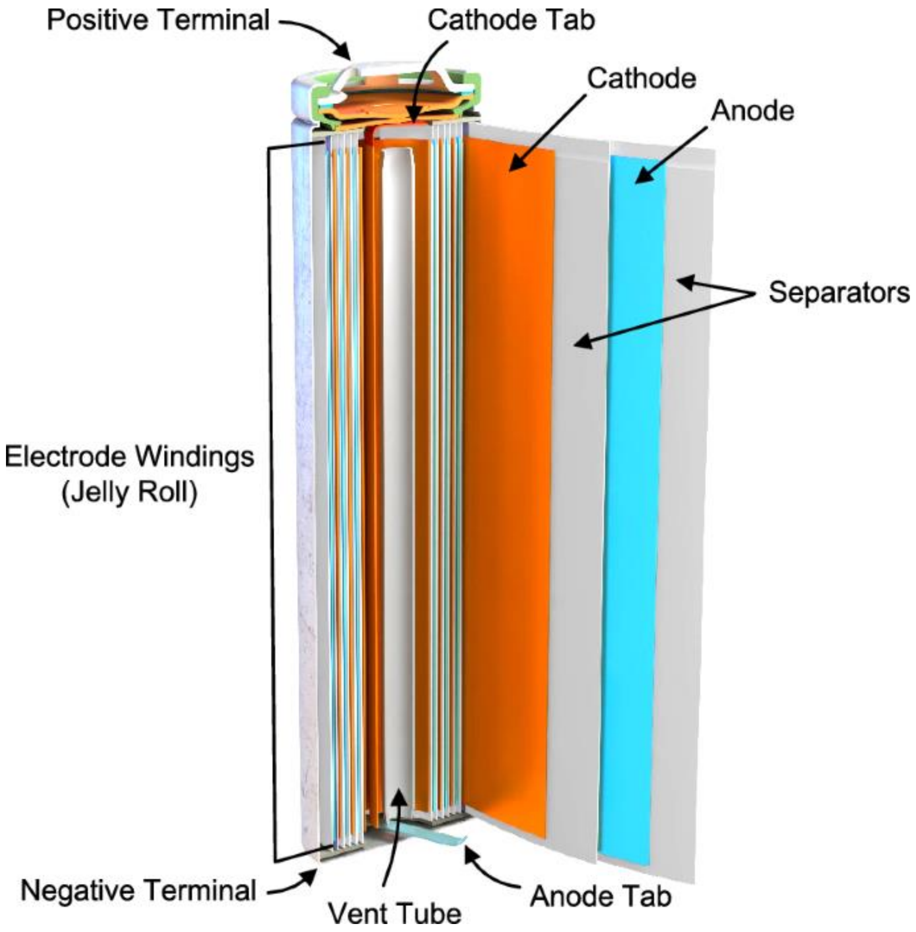
John B. Goodenough *(USA, left)*, M. Stanley Whittingham *(UK, centre)*, and Akira Yoshino *(JPN, right)* share the Nobel Prize for the development of lithium-ion batteries

Why lithium?

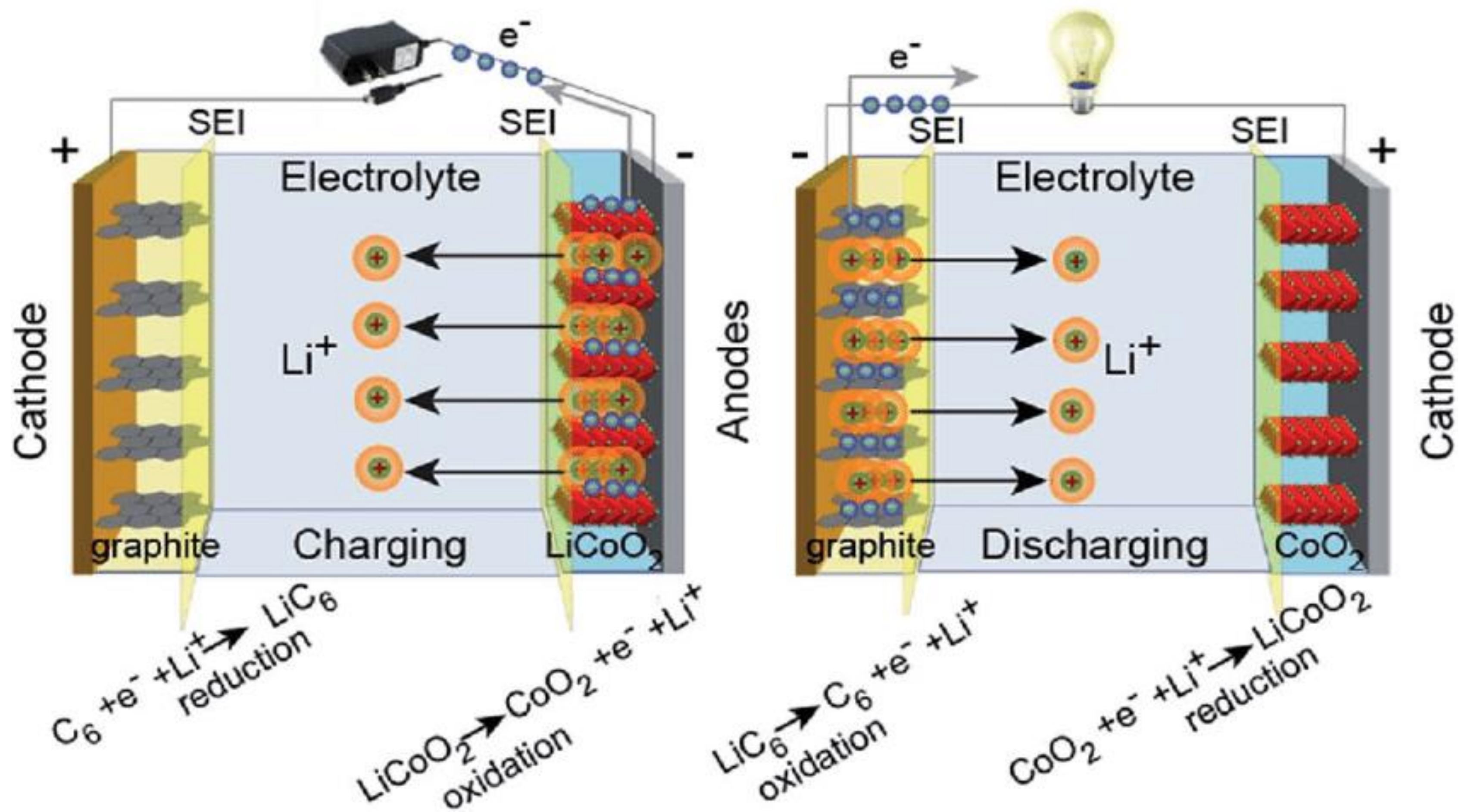
- Currently, most portable electronic devices, including cell phones and laptop computers, are powered by rechargeable lithium-ion (Li-ion) batteries, because:
- Lithium is a very light element.
- Li-ion batteries achieve a high specific energy density which is the amount of energy stored per unit mass.
- Because Li^+ has a very large negative standard reduction potential, Li-ion batteries produce a higher voltage per cell than other batteries.
- 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.
- 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. Polyethylene (PE), polypropylene (PP), and PE/PP separators with pore sizes are used.



Charging Reaction and Discharging



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

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

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-Cad 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 decompose to form CO_2 which causes pressure build up in battery, resulting in a dangerous explosion.

Batteries Vs Capacitors

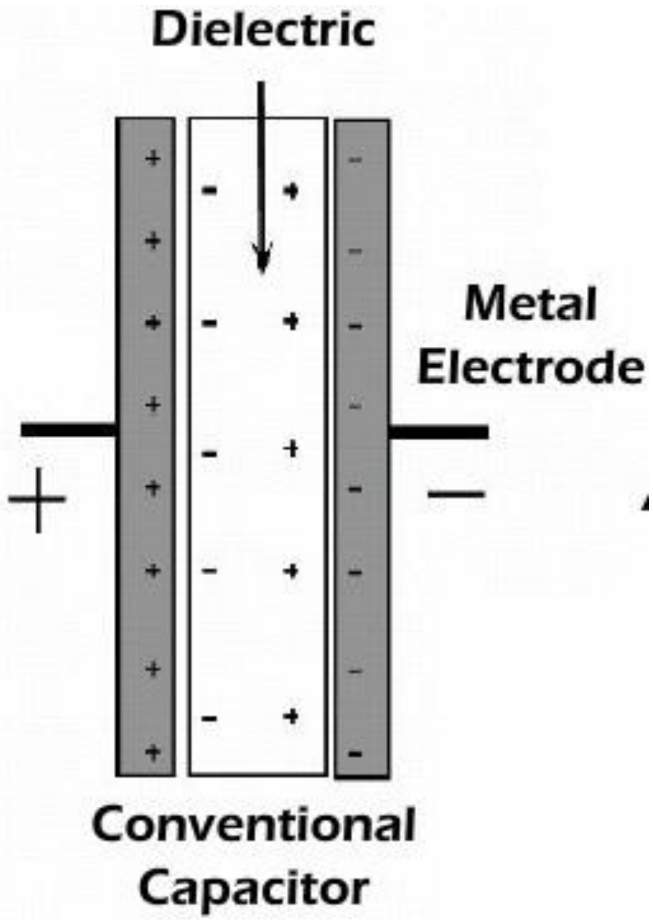
- Batteries and capacitors do a similar job—storing electricity—but in completely different ways. Batteries have two electrical terminals (electrodes) separated by a chemical substance called an electrolyte.
- When power is on, chemical reactions happen involving both the electrodes and the electrolyte. These reactions convert the chemicals inside the battery into other substances, releasing electrical energy as they go. Once the chemicals have all been depleted, the reactions stop and the battery is flat.

- A supercapacitor is a type of capacitor that can store a large amount of energy, typically 10 to 100 times more energy per unit mass or volume compared to electrolytic capacitors.
- These can deliver and accept charge more quickly than batteries.

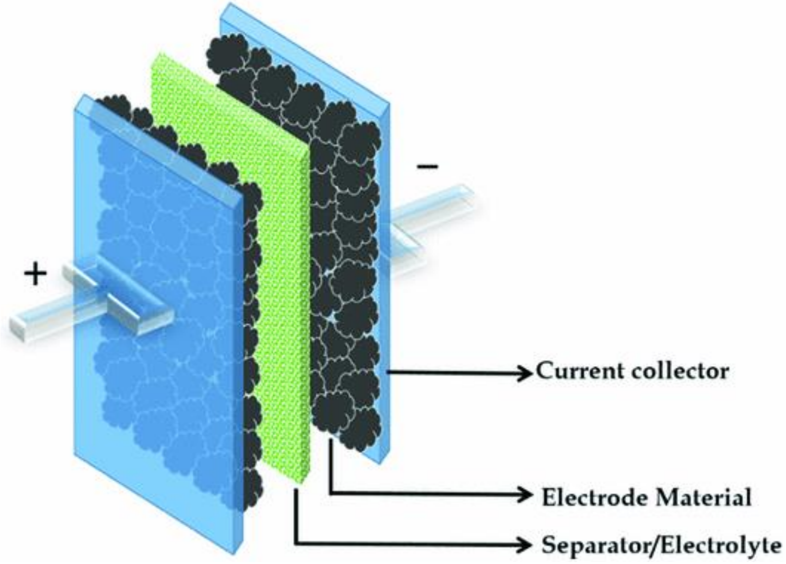
Supercapacitors/ Ultracapacitors

Capacitors

- A capacitor is a device used to store electrical charge and electrical energy.
- Capacitors use static electricity (electrostatics) rather than chemical substances to store energy.
- Inside a capacitor, there are two conducting metal plates with an insulating material called a dielectric in between them - it's a dielectric sandwich.
- Positive and negative electrical charges build up on the plates and the separation between them, which prevents them coming into contact, is what stores the energy.
- The dielectric allows a capacitor of a certain size to store more charge at the same voltage, so it makes the capacitor more efficient as a charge-storing device.

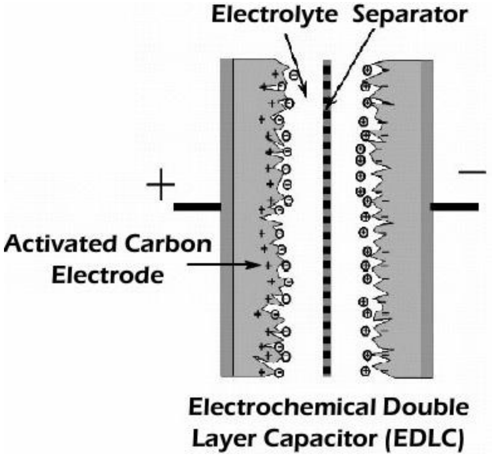


- A supercapacitor differs from an ordinary capacitor in two important ways:
  - Its plates effectively have a much bigger area and the distance between them is much smaller, because the separator between them works in a different way to a conventional dielectric.
  - Although the words "supercapacitor” and "ultra capacitor” are often used interchangeably, there is a difference: they are usually built from different materials and structured in slightly different ways, so they store different amounts of energy.
- Like an ordinary capacitor, a supercapacitor has two plates that are separated.
- The plates are made from metal coated with a porous substance such as powdery, activated charcoal, which effectively gives them a bigger area for storing much more charge. Unlike capacitor, in a supercapacitor, there is no dielectric as such. Instead, both plates are soaked in an electrolyte and separated by a very thin insulator (which might be made of carbon, paper, or plastic)

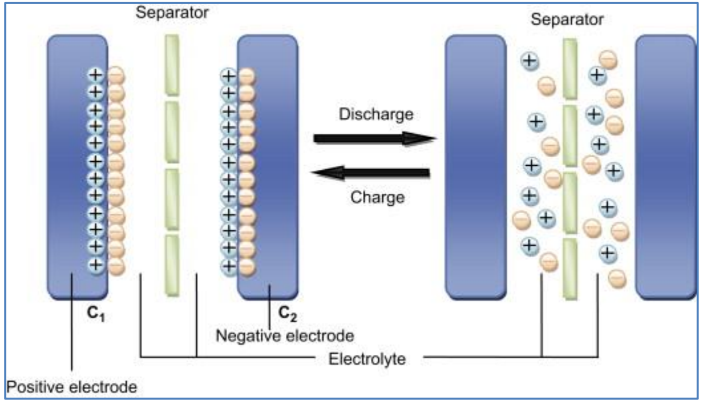


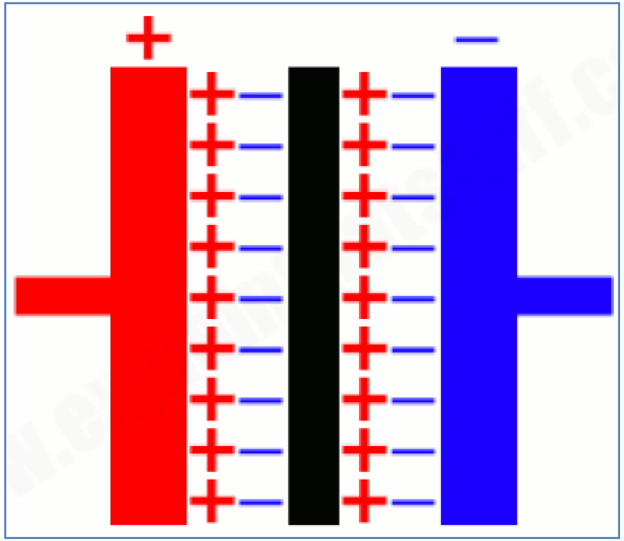
How do Supercapacitors Work?

- When the plates are charged up, an opposite charge forms on either side of the separator, creating what's called an electric double-layer.
- This is why supercapacitors are often referred to as double-layer capacitors, also called electric double-layer capacitors or EDLCs).
- The capacitance of a capacitor increases as the area of the plates increases and as the distance between the plates decreases.



Electrochemical Double Layer Capacitor (EDLC)



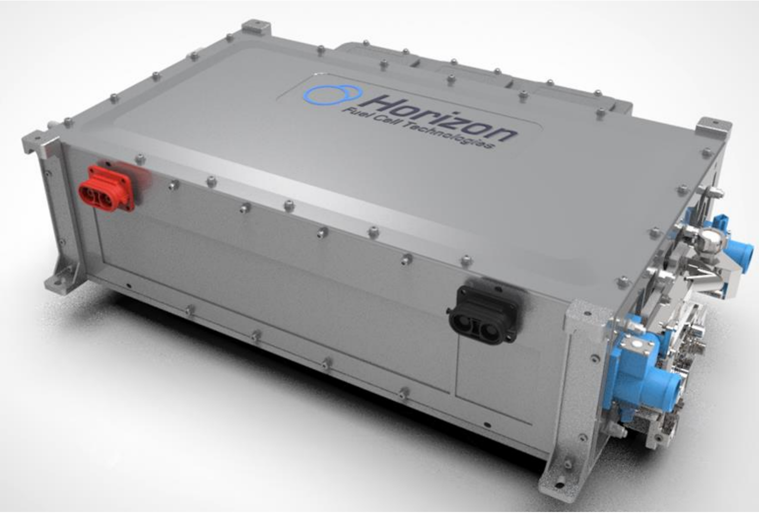


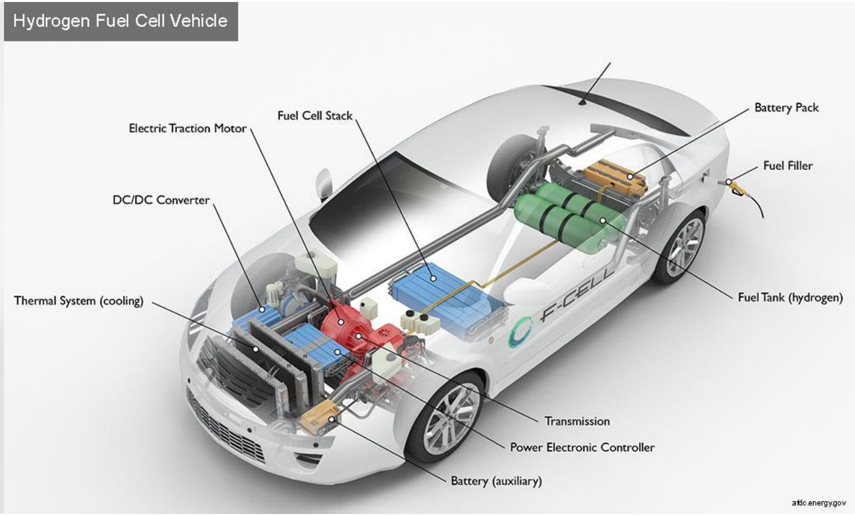
Application of Supercapacitors

- Supercapacitors have been widely used as the electrical equivalents of flywheels in machines—"energy reservoirs" that smooth out power supplies to electrical and electronic equipment.
- Supercapacitors can also be connected to batteries to regulate the power they supply.
- In wind turbines, where very large supercapacitors help to smooth out the intermittent power supplied by the wind. In electric and hybrid vehicles, supercapacitors are increasingly being used as temporary energy stores for regenerative braking (where the energy a vehicle would normally waste when it comes to a stop is briefly stored and then reused when it starts moving again).

Fuel Cells

- A fuel cell is a device that converts chemical potential energy (energy stored in molecular bonds) into electrical energy without combustion.
- They offer higher electrical efficiency (≥ 40%) compared to conventional power generation systems.





Principle of Operation

- A fuel cell is a device that uses hydrogen (or hydrogen-rich fuel) and oxygen to create electricity by an electrochemical process.
- Hydrogen and oxygen (air) are supplied to anode and cathode, respectively.
- When hydrogen is led to the anode, the hydrogen molecules are split into proton and an electron. The protons migrate through the electrolyte to the cathode, where they react with oxygen to form water.
- At the same time, the electrons are forced to travel around the electrolyte to the cathode side, because they cannot pass through the electrolyte. This movement of electrons thus creates an electrical current.

Types of Fuel Cells

- There are eight main types of fuel cells, based mainly on the type of electrolyte:
  - PEMFCs, proton exchange membrane or polymer electrolyte membrane fuel cells
  - AFCs, alkaline fuel cells
  - PAFCs, phosphoric acid fuel cells
  - MCFCs, molten carbonate fuel cells
  - SOFCs, solid oxide fuel cells
  - DMFCs, direct methanol fuel cells
  - DAFCs, direct ammonia fuel cells
  - DCFCs, direct carbon fuel cells
- Apart from DAFCs, DMFCs, and DCFCs, other types of fuel cells are fed with hydrogen.

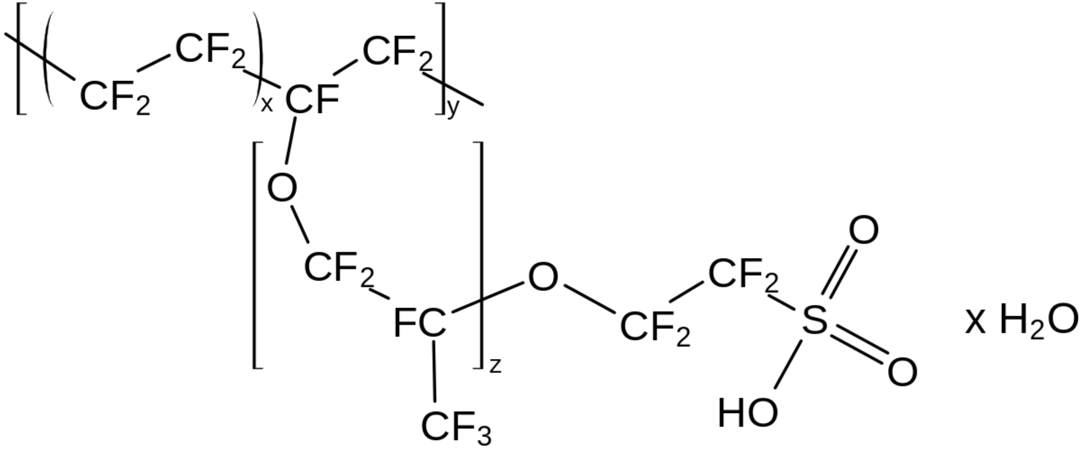
Hydrogen – oxygen fuel cells (HOFC)

- This cell is a common type of fuel cell. Similar to a galvanic cell, fuel cells also have two half cells.
- Both half cells have porous graphite electrode with a catalyst (platinum, silver or a metal oxide).
- The electrodes are placed in the aqueous solution of NaOH or KOH (alkaline fuel cells-AFC) or H_2SO_4 (acidic fuel cell) which acts as an electrolyte.
- Hydrogen and oxygen are supplied at anode and cathode respectively at about 50 atmospheric pressure, the gases diffuse at respective electrodes.
- The overall chemical reaction in a hydrogen fuel electrochemical cell involves the oxidation of hydrogen by oxygen to produce only water.

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

Proton exchange membrane fuel cell (PEMFC)
or
Polymer electrolyte membrane fuel cells (PEMFC)

- This type of fuel cell utilize water-based, acidic polymer electrolyte membranes (PEMs), such as Nafion, to conduct protons for ion exchange purposes.
- PEMFC cells operate at relatively low temperatures (< 80°C).
- Due to the relatively low temperatures and the use of precious metal-based electrodes, these cells must be operated on pure hydrogen.



Nafion

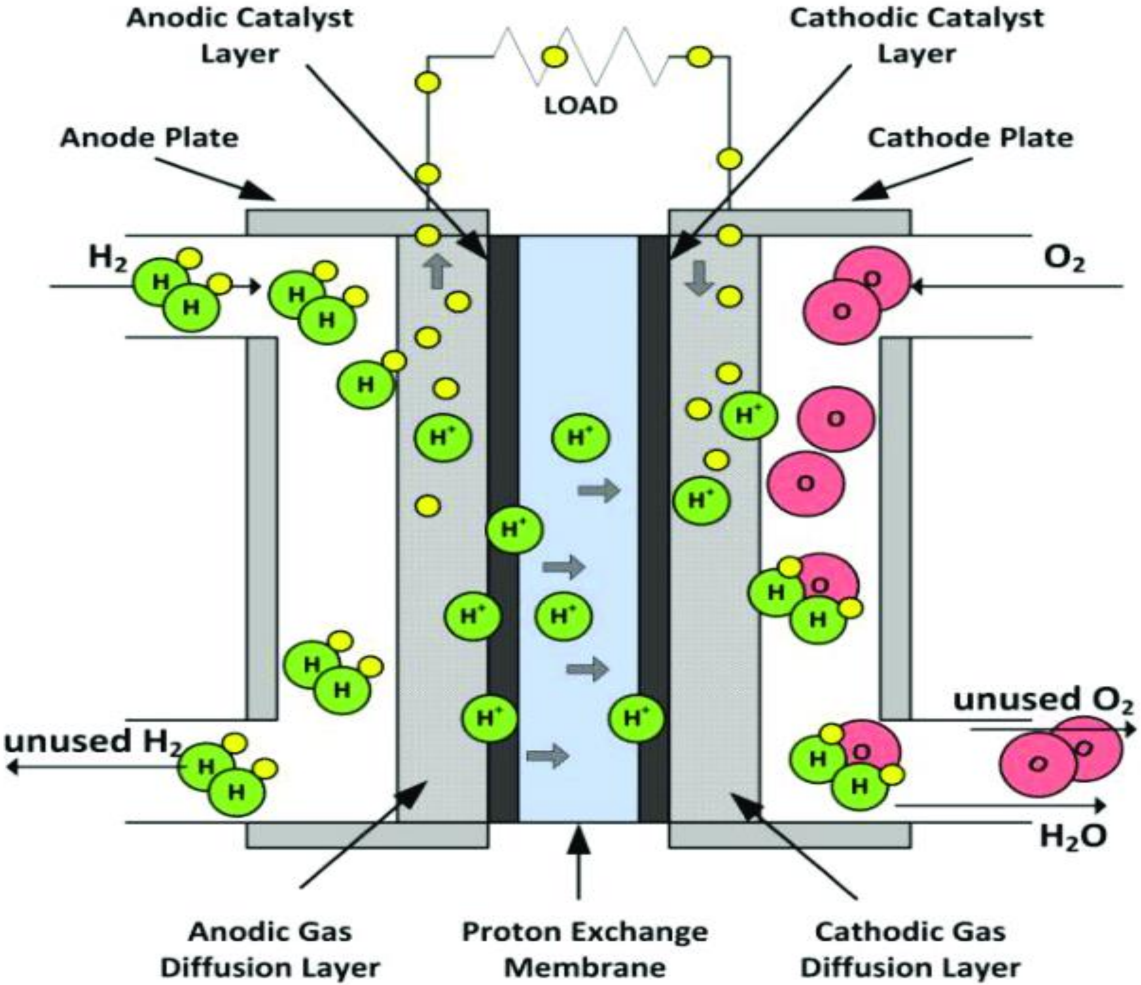
Process

- Hydrogen fuel is processed at the anode where electrons are separated from protons on the surface of a platinum-based catalyst.
- The protons pass through the membrane to the cathode side of the cell while the electrons travel in an external circuit, generating the electrical output of the cell.
- On the cathode side, another Pt electrode combines the protons and electrons with oxygen to produce water.

- **At anode:** $H_2\,(g) \rightarrow 2\,H^+ + 2\,e^-$
- **At cathode:** $O_2\,(g) + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$
- **Net reaction:** $O_2\,(g) + 2\,H_2\,(g) \rightarrow 2\,H_2O\,(l)$

$$E_{Cell}^{\circ} = 1.23\ V$$

PEMFC


Anodic Catalyst Layer
LOAD
Cathodic Catalyst Layer
Anode Plate
Cathode Plate
H₂
O₂
H
O
H⁺
unused H₂
unused O₂
H₂O
Anodic Gas Diffusion Layer
Proton Exchange Membrane
Cathodic Gas Diffusion Layer

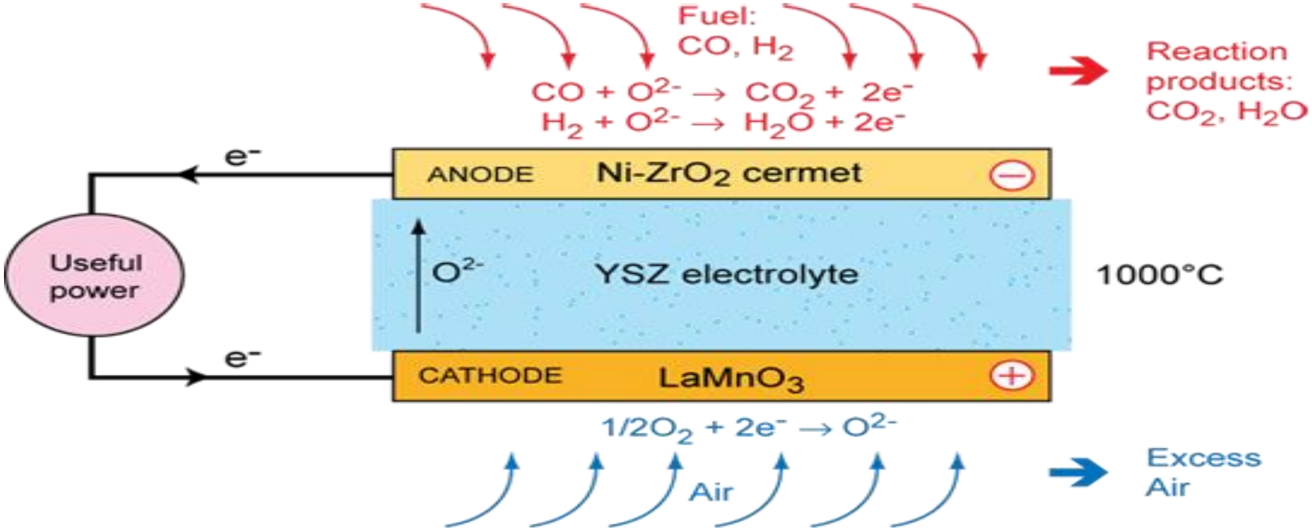
- **Advantages**
  - The energy conversion is very high (75-82%).
  - Fuel cell minimizes expensive transmission lines and transmission losses.
  - It has high reliability in electricity generation and the by-products are environmentally acceptable.
  - Maintenance cost is low for these fuels and they save fossil fuels.
  - Noise and thermal pollution are very low.
- **Disadvantages:**
  - The major disadvantage of the fuel cell is the high cost and the problems of durability and storage of large amount of hydrogen.
  - The accurate life time is also not known and It cannot store electricity.
  - Electrodes are expensive and short lived.
  - Storage and handling of H_2 gas is dangerous because it is inflammable.
- **Applications:**
  - The most important application of a fuel cell is its use in space vehicles, submarine or military vehicles.
  - The product H_2O is valuable source of fresh water for the astronauts.
  - Fuel cell batteries for automotive will be a great boon for the future.

Solid Oxide Fuel Cell (SOFC)

- SOFC is a high-temperature FC that utilizes solid ceramic inorganic oxide as an electrolyte; e.g., zirconium oxide stabilized with yttrium oxide, instead of a liquid or membrane, also known as Yttria-stabilized Zirconia (YSZ).
- SOFC is also referred to as ceramic FC.
- Both hydrogen and carbon monoxide are used as fuels.
- Solid oxide fuel cells work at very high temperatures, the highest of all the fuel cell types at around 800 °C to 1,000 °C.
- Efficiency: over 60% when converting fuel to electricity
- This cell is relatively resistant to small quantities of sulphur in the fuel, compared to other types of fuel cell, and hence can be used with coal gas.

Structure of SOFC

- **Anode or fuel electrode:**
  - Nickel mixed with YSZ (Yttria stabilized Zirconia) or called Nickel-YSZ cermet (a cermet is a mixture of ceramic and metal).
  - It is a porous ceramic layer to allow the fuel to flow towards electrolyte.
- **Cathode or air electrode:**
  - The cathode is usually a mixed ion-conducting and electronically conducting ceramic material.
  - It is a thin porous ceramic layer coated over the solid electrolyte where oxygen reduction takes place. One example being, strontium doped lanthanum manganite (LSM).
- **Electrolyte:**
  - Oxide ion (O^{2-}) conducting ceramic.
  - The most popular electrolyte material is a bilayer composite electrolyte (YSZ layer + gadolinium doped CeO_2) (GDC) layer) or a mixture of ZrO and CaO.



- **At anode (oxidation):**

$$H_2\,(g) + CO\,(g) + 2\,O^{2-} \rightarrow H_2O\,(g) + CO_2\,(g) + 4e^-$$

- **At cathode (reduction):**

$$O_2\,(g) + 4e^- \rightarrow 2\,O^{2-}$$

- **Net reaction:**

$$H_2\,(g) + CO\,(g) + O_2\,(g) \rightarrow H_2O\,(g) + CO_2\,(g)$$

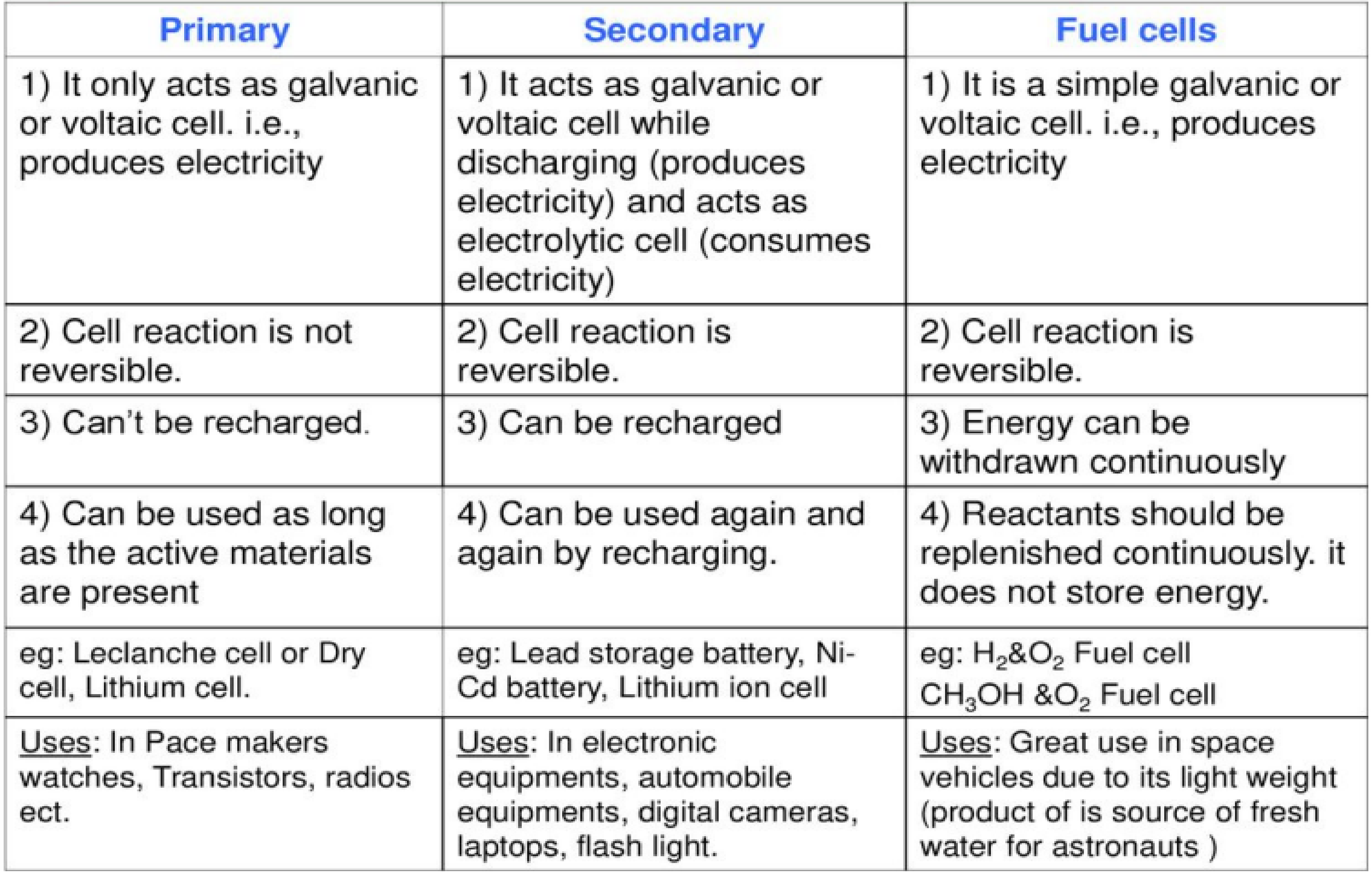
Advantages of SOFC:

- SOFCs have a number of advantages due to their solid materials and high operating temperature.
- Since all the components are solid, as a result, there is no need for electrolyte loss maintenance and electrode corrosion is eliminated.
- Also because of high-temperature operation, the SOFC has a better ability to tolerate the presence of impurities as a result of life increasing.
- **High efficiencies:** Due to high-quality waste heat for cogeneration applications and low activation losses, the efficiency for electricity production is great.
- Low emissions. Releasing negligible pollution. It is the cleanest among all fuel cells.

- **Disadvantages:**
  - **High operating temperature (500 to 1,000 °C) which results in longer start up times and mechanical/chemical compatibility issues.**
  - **The cost and complex fabrication are also significant problems that need to be solved.**

- **Applications:**
  - **SOFCs are being considered for a wide range of applications, such as working as power systems for trains, ships and vehicles; supplying electrical power for residential or industrial utility.**
  - **Stationary power generation**
  - **By product gases are channeled to turbines to generate more electricity: cogeneration of heat and power and improves overall efficiency.**
  - **Auxiliary power units in vehicles**

Differences between Primary, Secondary and Fuel cells



Primary	Secondary	Fuel cells
1) It only acts as galvanic or voltaic cell. i.e., produces electricity	1) It acts as galvanic or voltaic cell while discharging (produces electricity) and acts as electrolytic cell (consumes electricity)	1) It is a simple galvanic or voltaic cell. i.e., produces electricity
2) Cell reaction is not reversible.	2) Cell reaction is reversible.	2) Cell reaction is reversible.
3) Can't be recharged.	3) Can be recharged	3) Energy can be withdrawn continuously
4) Can be used as long as the active materials are present	4) Can be used again and again by recharging.	4) Reactants should be replenished continuously. it does not store energy.
eg: Leclanche cell or Dry cell, Lithium cell.	eg: Lead storage battery, Ni-Cd battery, Lithium ion cell	eg: H_2&O_2 Fuel cell CH_3OH &O_2 Fuel cell
Uses: In Pace makers watches, Transistors, radios ect.	Uses: In electronic equipments, automobile equipments, digital cameras, laptops, flash light.	Uses: Great use in space vehicles due to its light weight (product of is source of fresh water for astronauts)

Solar Energy Potential

- **Theoretical:** $1.2\text{x}10^5$ TW solar energy potential
  ($1.76\ \text{x}10^5$ TW striking Earth; 0.30 Global mean albedo)

  Energy in 1 hr of sunlight ↔ 14 TW for a year

- **Practical:** ≈ 600 TW solar energy potential (50 TW - 1500 TW depending on land fraction etc.; WEA 2000)

  Onshore electricity generation potential of ≈ 60 TW (10% conversion efficiency)
  Photosynthesis: 90 TW

Solar energy conversion devices

Methods of tapping solar energy

A. Photosynthesis
Plants
(Visible light)
η = 2-4%

B. Water heaters
Flat plate, tube
(IR radiation)

C. Photovoltaic cells
p/n Si, Si, GaAs
(Visible light)
η = 12-26%

D. Chemical routes

- D1: Biomimetism
  Mimicking
  Photosynthesis
  via chemicals
- D2: PEC cells
  - a. LJSC
    - (i) Sc/Elect/M
      η= 13-14%
    - (ii) Photogalvanic cells
      M/Elect/M
      η= 0.01%
  - b. Photoelectrosynthesis (PES) cells
    - (i) Photoassisted electrolysis cells
      η= 13.3%
    - (ii) Photoassisted electrosynthesis cells
      eg. $CO_2 \rightarrow CH_3OH$
      $N_2 \rightarrow NH_3$

Types of solar energy conversion cells

- Photovoltaic Cells
- Photoelectrochemical cells
- Dye-sensitized solar cells

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.

Why Silicon?

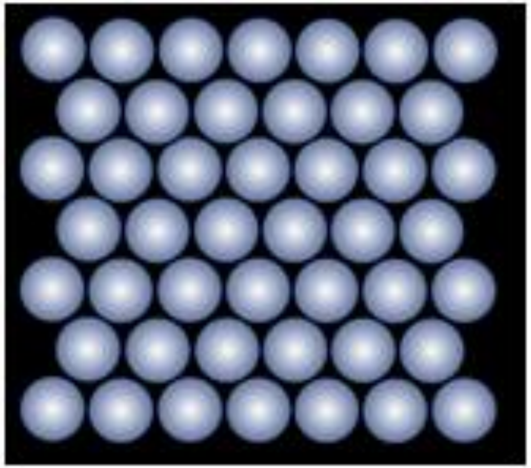
Silicon is considered as the most suitable material for solar energy conversion because:

- Second most abundant element (~ 28% by mass) after oxygen
- Highly pure silicon can be readily synthesized from sand or quartz by heating them at high temperature in furnace

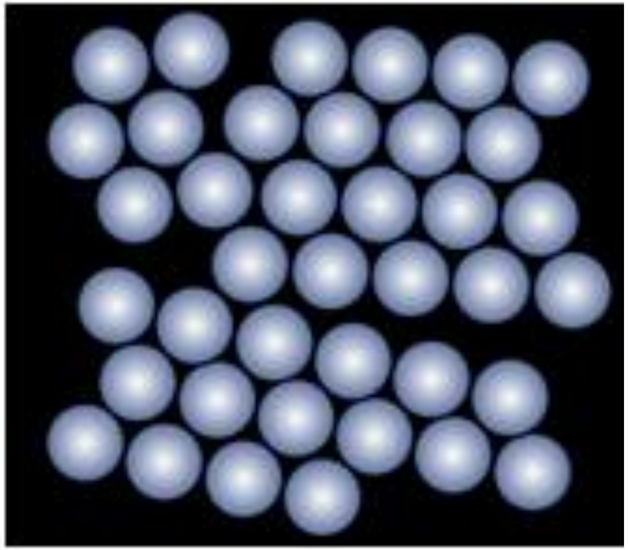
$$SiO_2 + C \rightarrow Si + CO_2$$

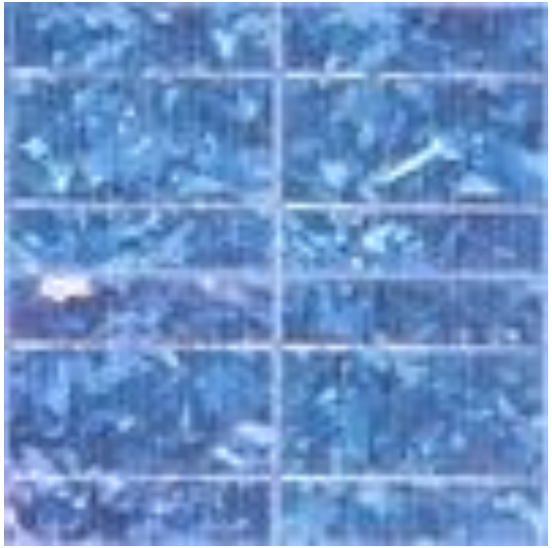
- Silicon is an excellent semiconductor with optimum band gap of 1.23 eV at 300 K
- Cost effectiveness
- Silicon can be easily doped with phosphorus (P), arsenic (As), antimony (Sb), boron (B), indium (In) or aluminium (Al).

- **Types PV based on the structure of silicon:** Crystal structure, or atomic arrangement in a material plays crucial role in its electrical properties.
  - **Single-crystal silicon:**
    - In its crystalline form, a material is characterized by an ordered array of component atoms. This array is repetitive with displacement through the material sample.
    - 15–18% efficient, typically expensive to make (grown as big crystal)

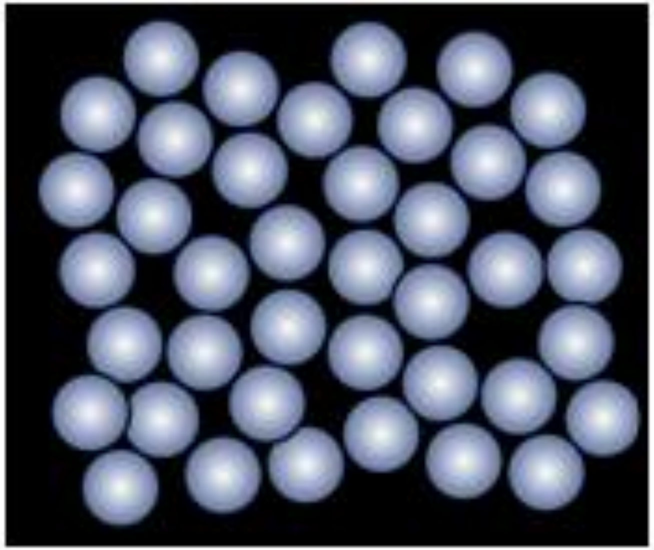


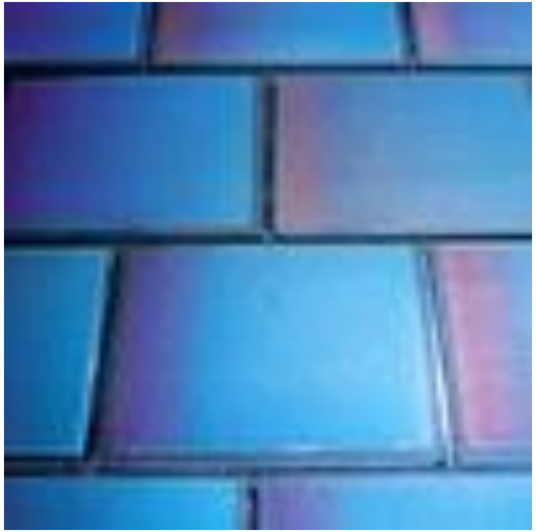
- **Poly-crystalline silicon:**
  - Where a polycrystalline material is concerned, the object is composed of a number of sub-sections, each of which is crystalline in form. These subsections, however, are independently oriented so that at their interfaces the atomic order and regularity undergo sharp discontinuities.
  - 12–16% efficient, slowly improving and cheaper to make (cast in ingots)



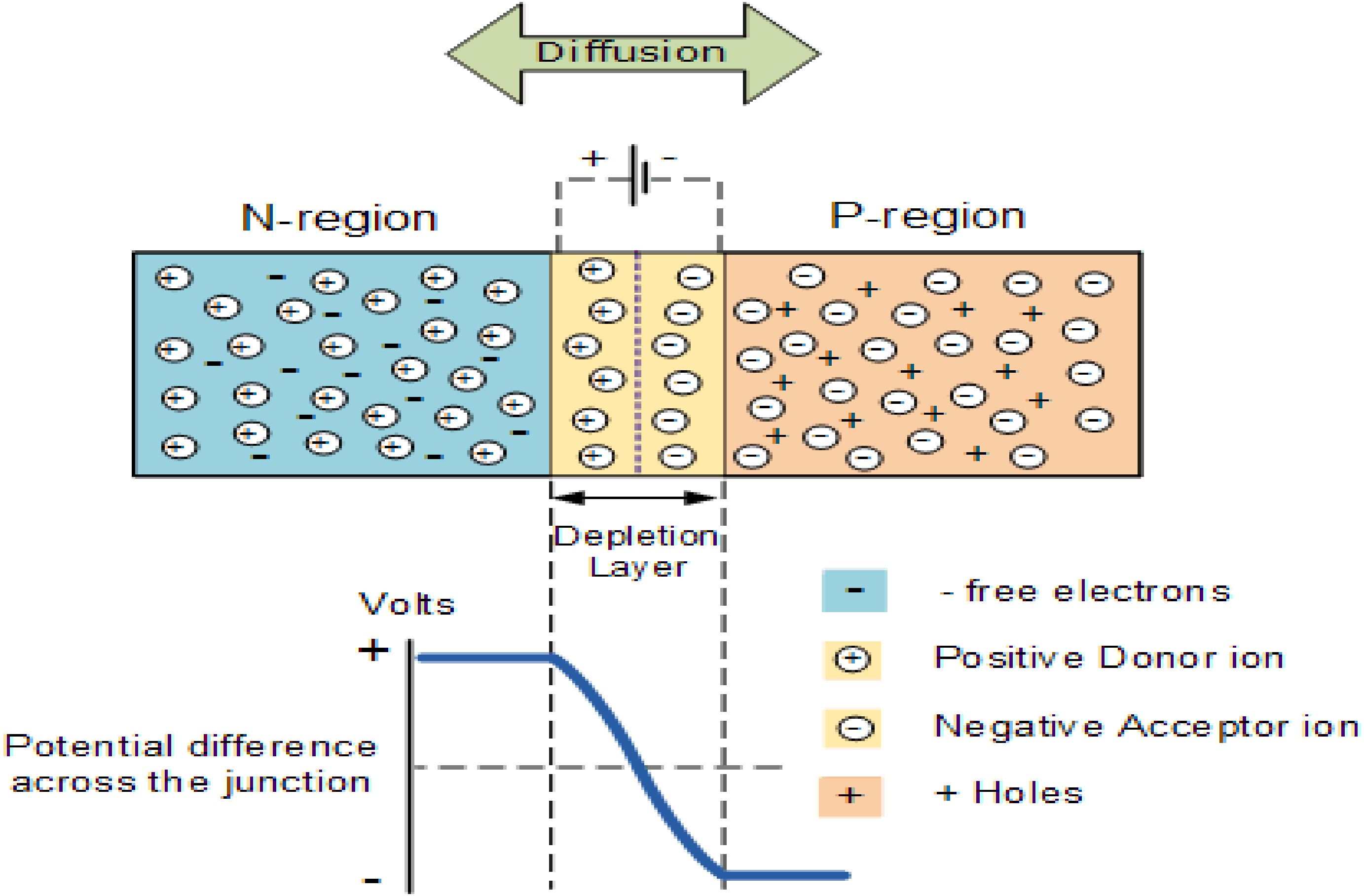


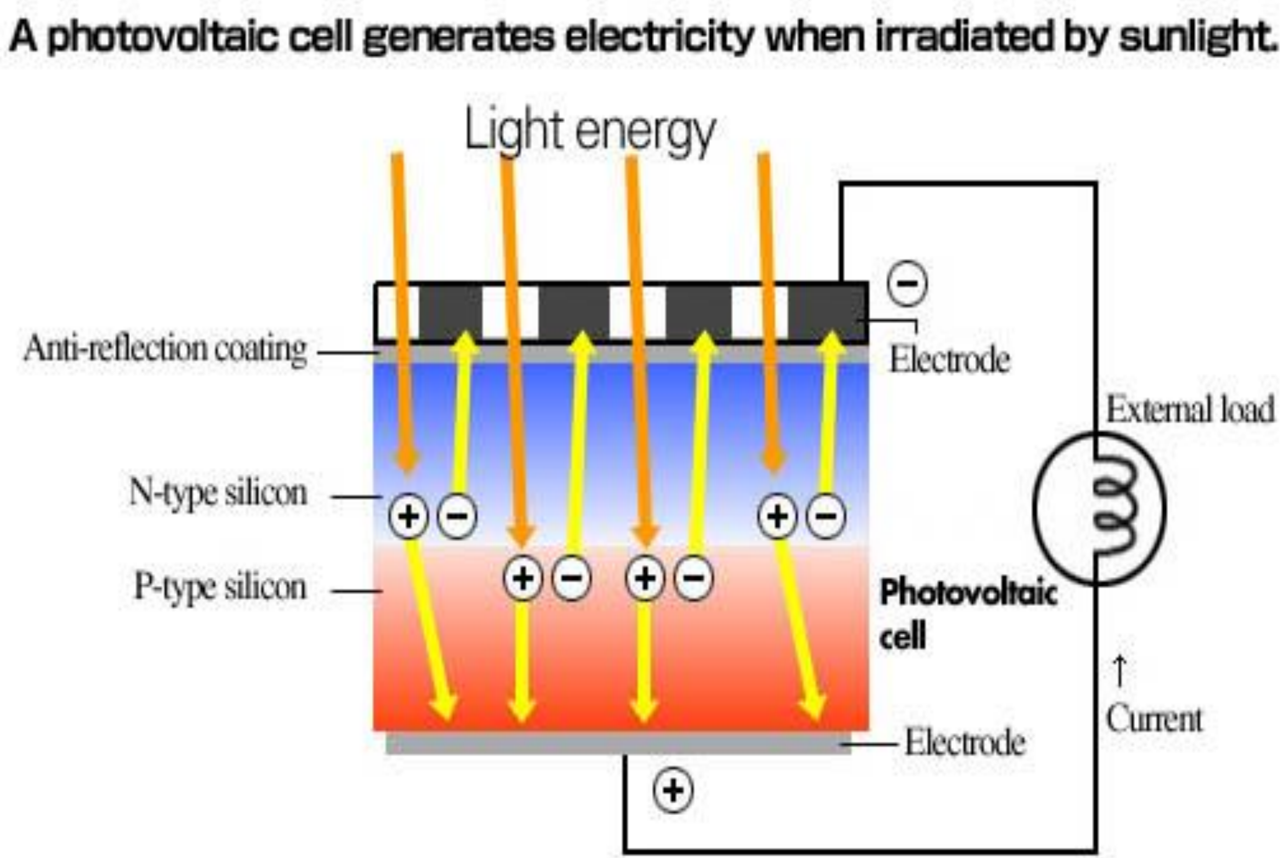
- **Amorphous silicon (non-crystalline)**
  - **The final category, the amorphous material, displays no atomic regularity of arrangement on any macroscopic scale.**
  - **4–8% Efficient and cheapest per Watt**
  - **Called as “thin film” and easily deposited on a wide range of surface types**



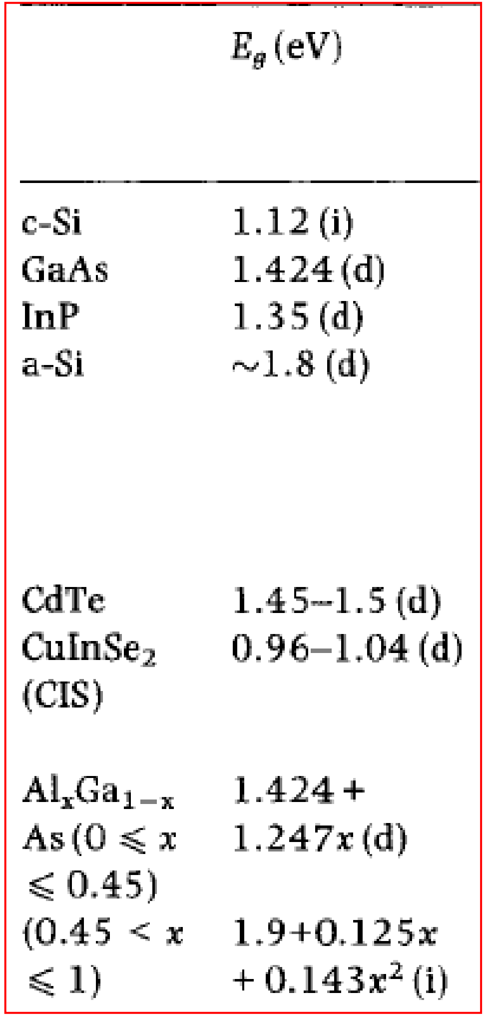


p-n junction

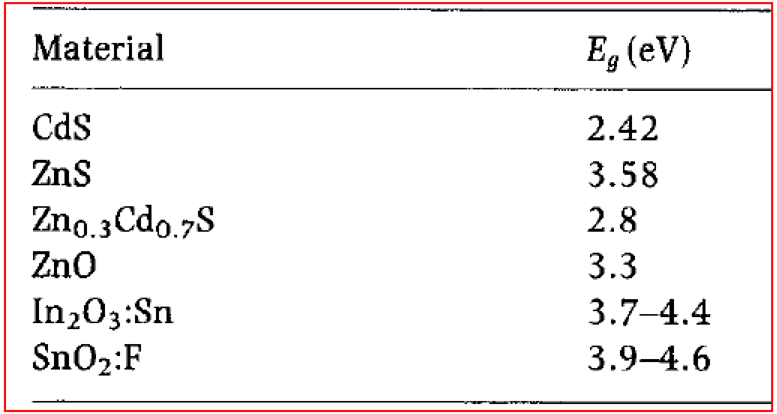

Diffusion
+
-
N-region
P-region
Depletion Layer
Volts
+
-
Potential difference across the junction
- free electrons
Positive Donor ion
Negative Acceptor ion
+ Holes



- System converts light energy to electricity
- Applications in Aerospace & Satellite etc



	E_g (eV)
c-Si	1.12 (i)
GaAs	1.424 (d)
InP	1.35 (d)
a-Si	~1.8 (d)
CdTe	1.45–1.5 (d)
$CuInSe_2$ (CIS)	0.96–1.04 (d)
$Al_xGa_{1-x}As$ ($0 \leqslant x \leqslant 0.45$)	$1.424 + 1.247x$ (d)
($0.45 < x \leqslant 1$)	$1.9+0.125x + 0.143x^2$ (i)



Material	E_g (eV)
CdS	2.42
ZnS	3.58
$Zn_{0.3}Cd_{0.7}S$	2.8
ZnO	3.3
In_2O_3:Sn	3.7–4.4
SnO_2:F	3.9–4.6

Disadvantages of Photovoltaic Solar Cells

- Some toxic chemicals, like cadmium and arsenic, are used in the PV production process. These environmental impacts are minor and can be easily controlled through recycling and proper disposal.
- The conversion of light energy into heat energy is one of the limitations.
- Solar energy is somewhat more expensive to produce than conventional sources of energy due in part to the cost of manufacturing PV devices
- Solar power is a variable energy source, with energy production dependent on the sun.
- Solar panels efficiency levels are relatively low (between 14%-25%) compared to the efficiency levels of other renewable energy systems.
- Solar panels are fragile and can be damaged relatively easily.

Photoelectrochemical cells

- Photoelectrochemical cell is a photocurrent generated device which is made up of an electrolyte and a photoactive semiconductor electrode.
- Photoelectrochemical (PEC) cell is a device in which a photoactive semiconductor material is in contact with an electrolyte .
- Irradiation of the SC/electrolyte junction with light of energy > E_g, the band gap of the semiconductor, produces electron - hole pairs.
- The electron-hole pairs are spatially separated (due to the junction potential) to drive oxidation and reduction reactions in the system.

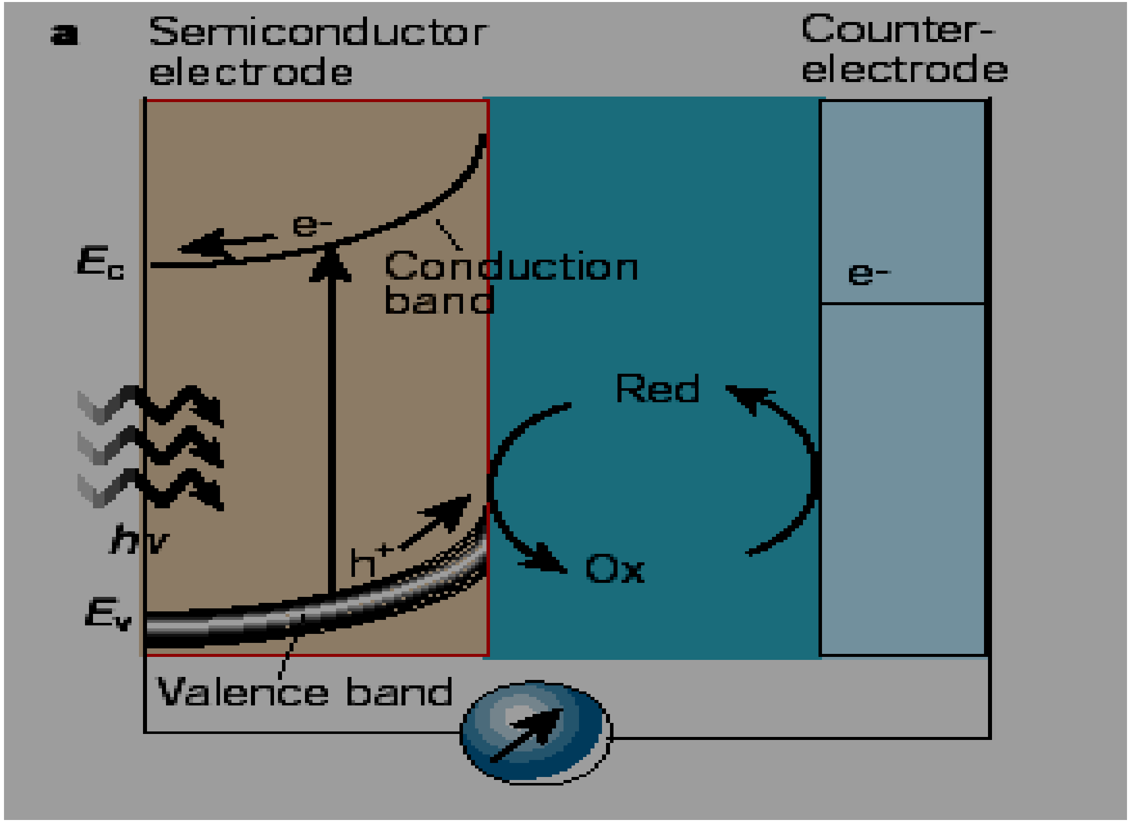
Photoelectrochemical cells

- **Types of Photoelectrochemical cells:**
  - **Liquid Junction Solar Cell (LJSC) – n-SC/Electrolyte/Metal**
  - **The free e-s in SC absorb the high energy radiation and then the excited e-s will move from the valance band to conduction band of the SC. As a result of this, the holes (+) are created.**

    This cell is used to convert solar energy into electrical energy.
  - **Photoelectrosynthesis (PES) cells –**

    In this class of cells, solar energy is converted into chemical energy in the form of fuels.

Regenerative photoelectrochemical cells



Major advantages of PEC cells over photovoltaic cells

- Easy junction formation (mere dipping of the SC electrode in the electrolyte).
- In-situ water electrolysis is possible.
- Efficiencies of polycrystalline bulk and thin film electrodes are comparable to those of single crystal electrodes.
- Novel reaction products are possible and catalytic effects (Photocatalysis) can be induced on the SC surfaces.
- Particulate systems can be used.

Conditions for Efficient Solar Energy Conversion – Electrodes

- The requirements for the electrode materials are:

(1) Band gap (E_g) should be optimum

(2) The doping level should be optimum, so that there will be a good spatial separation of the photo-generated carriers and hence, high quantum efficiency.

(3) Should have large values of absorption co-efficient (α). This is usually found for direct band gap SC's.

(4) Applied bias (external energy source) makes the LJSCs more efficient.

Working of PEC cells

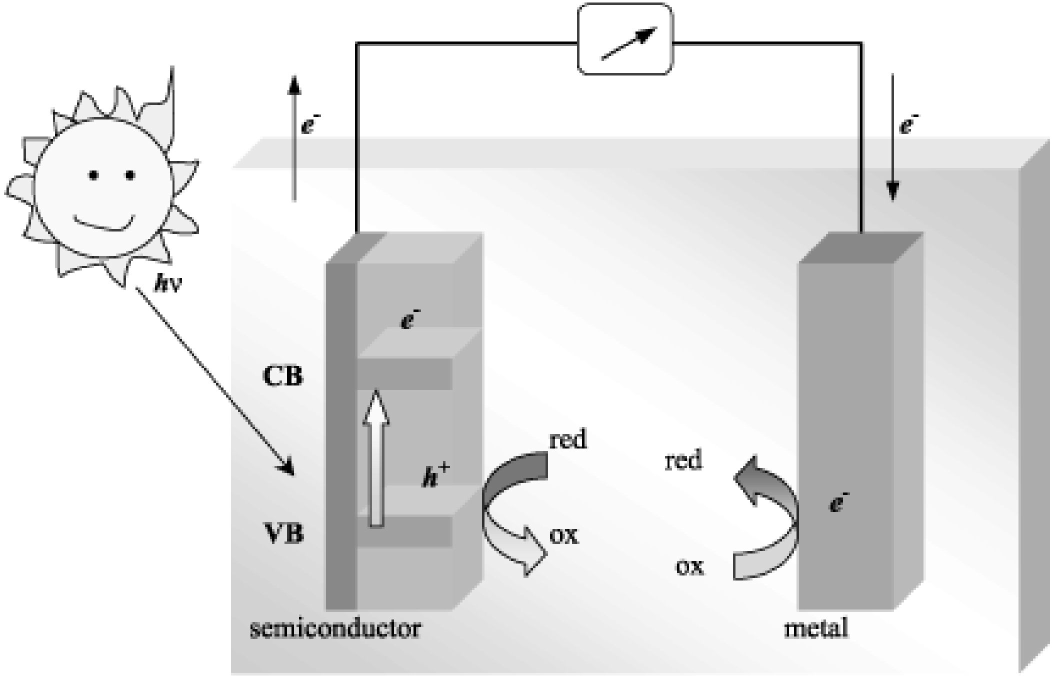


Figure 1. Representation of a semiconductor | liquid junction photovoltaic cell.

Dye Sensitization - Grätzel cell

1. **Sunlight energy (photon of light) passes through the titanium dioxide layer and strikes electrons within the adsorbed dye molecules. Electrons gain this energy and become excited because they have the extra energy.**
2. **The excited electrons escape the dye molecules and become free electrons. These free electrons move through the titanium dioxide and accumulate at the -ve plate (dyed TiO_2 plate).**
3. **The free electrons then start to flow through the external circuit to produce an electric current. This electric current powers the light bulb.**
4. **To complete the circuit, the dye is regenerated. The dye regains its lost electrons from the iodide electrolyte. Iodide (I^-) ions are oxidised (loss of 2 electrons) to tri-iodide (I_3^-). The free electrons on the graphite plate then reduce the tri-iodide molecules back to their iodide state. The dye molecules are then ready for the next *excitation/oxid/red* cycle.**

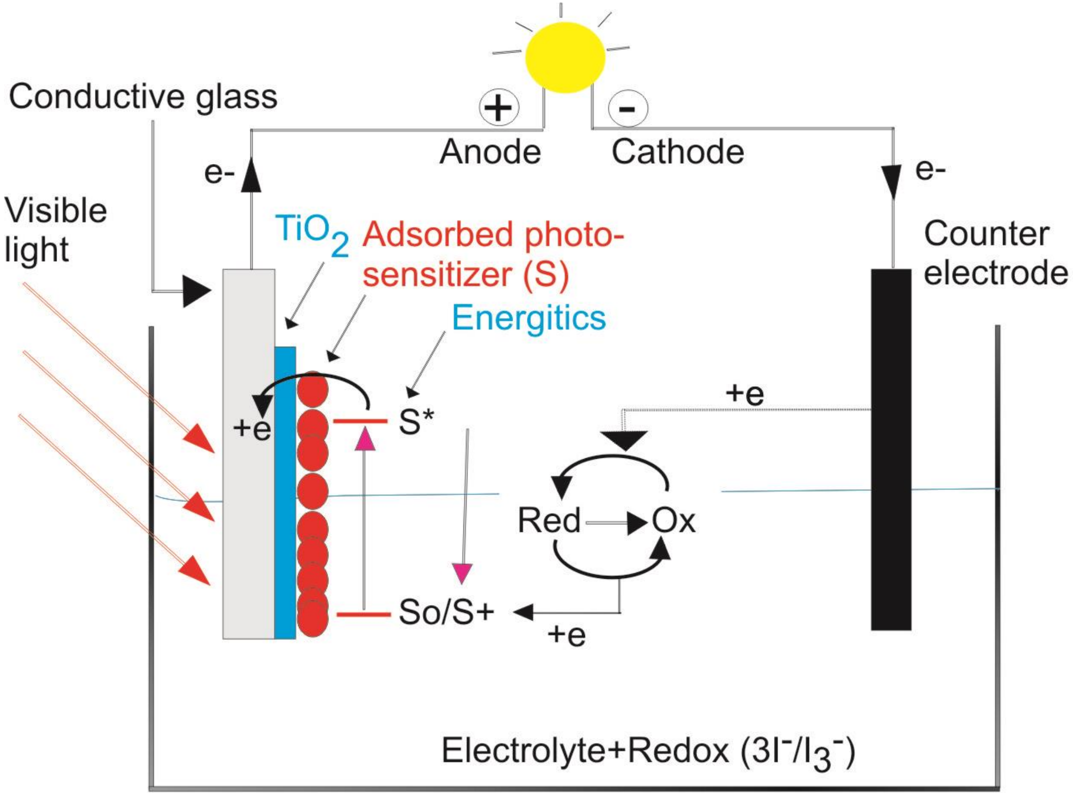


Photo-sensitizer (S) = $Ru(bpy)_3^{2+}$; bpy = bipyridyl legand

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

Transparent and Conductive Substrate

- Substrate for the deposition of the semiconductor and catalyst, acting also as current collectors
- Characteristics of a substrate:

  More than 80% of transparency

  Should have a high electrical conductivity.
- The fluorine-doped tin oxide (FTO, SnO_2: F) and indium-doped tin oxide (ITO, In_2O_3: Sn) are usually applied as a conductive substrate in DSSCs.
- These substrates consist of soda lime glass coated with the layers of ITO and FTO.
- The ITO films have a transmittance > 80% and 18 Ω /cm^2 of sheet resistance,
- FTO films show a lower transmittance of ~ 75% in the visible region and sheet resistance of 8.5 Ω /cm^2

Working Electrode (WE)

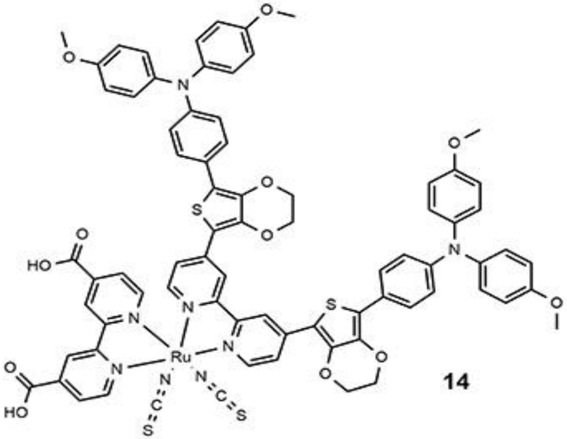
- Working electrodes (WE) are prepared by depositing a thin layer of oxide semiconducting materials such as TiO_2, Nb_2O_5, ZnO, SnO_2 (n-type), and NiO (p-type) on a transparent conducting glass plate made of FTO or ITO
- These oxides have a wide energy band gap of 3 – 3.2 eV
- Due to its non-toxicity, and easy availability, TiO_2 is mostly used as a semiconducting layer
- To enhance its activity the 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.

Photosensitizer or Dye

- **Dye are responsible for the maximum absorption of light.**
- **These should have the following photophysical and electrochemical properties:**
  - **Dyes should be luminescent.**
  - **Their absorption spectra should cover UV-vis and NIR regions.**
  - **The periphery of the dye should be hydrophobic to enhance the long-term stability of cells.**
  - **Co-absorbents like chenodeoxycholic acid (CDCA) or anchoring groups like alkoxy-silyl, phosphoric acid, and -COOH should be present to avoid the aggregation of the dye over the TiO_2 surface.**

- **Electrolyte**
  - An electrolyte, such as I^-/I_3^-, Br^-/Br_2^-, SCN^-/SCN_2, and Co(II)/Co(III) has five main components, i.e., redox couple, solvent, additives, ionic liquids, and cations.
  - The following properties should be present in an 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.
- **Counter Electrode (CE)**
  - CE in DSSCs are mostly prepared by using Pt, C, CoS, Au/GNP, alloy CEs like FeSe, and $CoNi_{0.25}$.

Photosensitizers or Dyes



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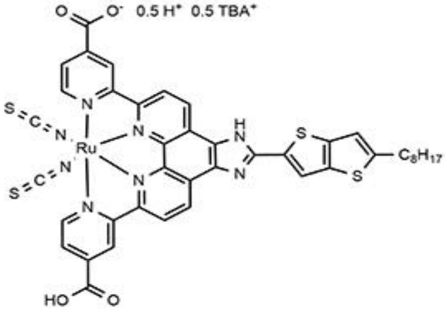

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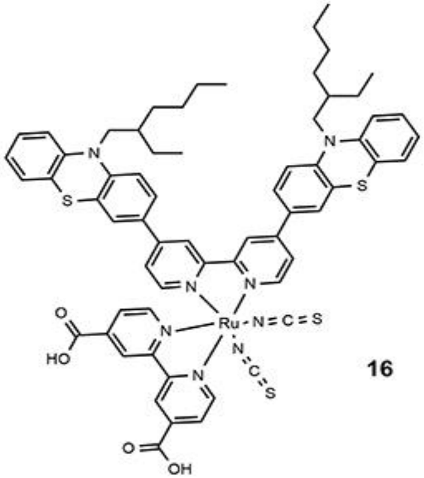

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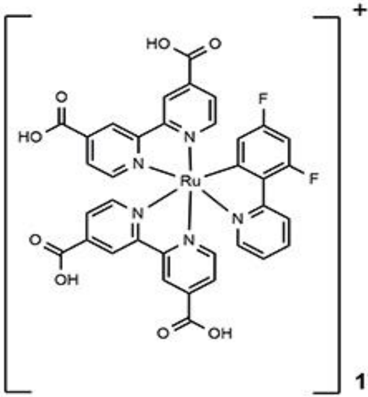

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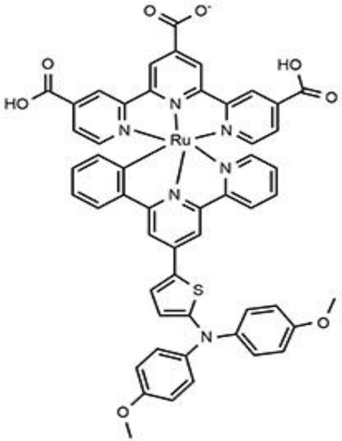

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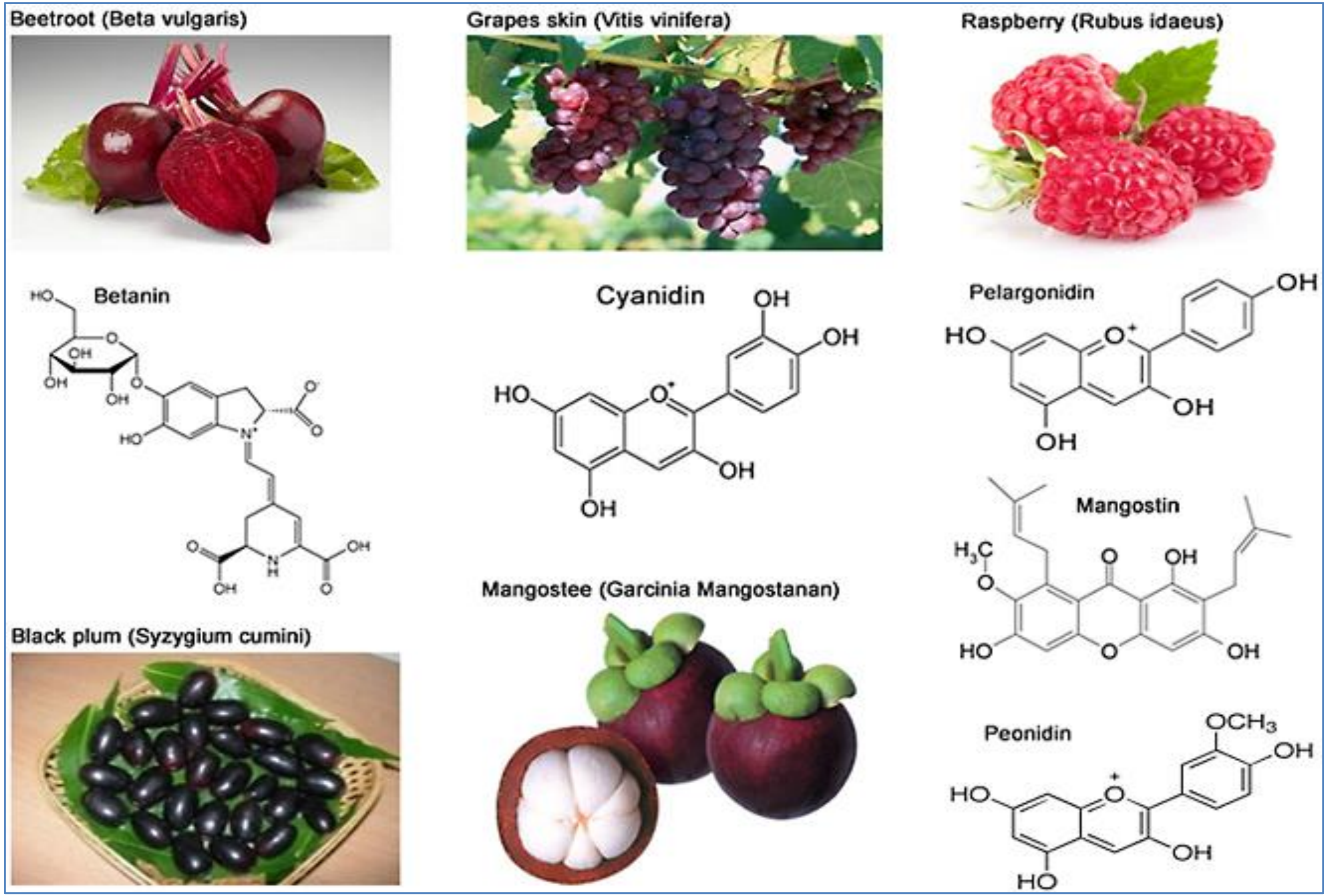
Naturally Occurring Dyes



Construction of a Grätzel cell

- In Grätzel cell a range of organic dyes are used.
- Examples: Ruthenium-Polypyridine, Indoline dye & metal free organic dye.
- These dyes are extractable from simple foods such as hibiscus tea, tinned summer fruits, blackberries.

Construction:

- Two transparent glass plates are perforated on one side with a transparent thin layer of a conducting material.
- Onto the conducting sides, one plate is coated with graphite and the other plate is coated with titanium dioxide (TiO_2).
- A dye is then adsorbed onto the TiO_2 layer by immersing the plate into a dye solution of 10^{-4}M in alcohol for 10 min. (approx.)
- The plates are then carefully sandwiched together and secured using a paper clip.
- To complete the cell a drop of iodide electrolyte is added between the plates.
- Figure shows a Grätzel cell prepared from hibiscus tea.
- The upper plate is the TiO_2 plate, dyed with hibiscus tea and the lower plate is coated with graphite.

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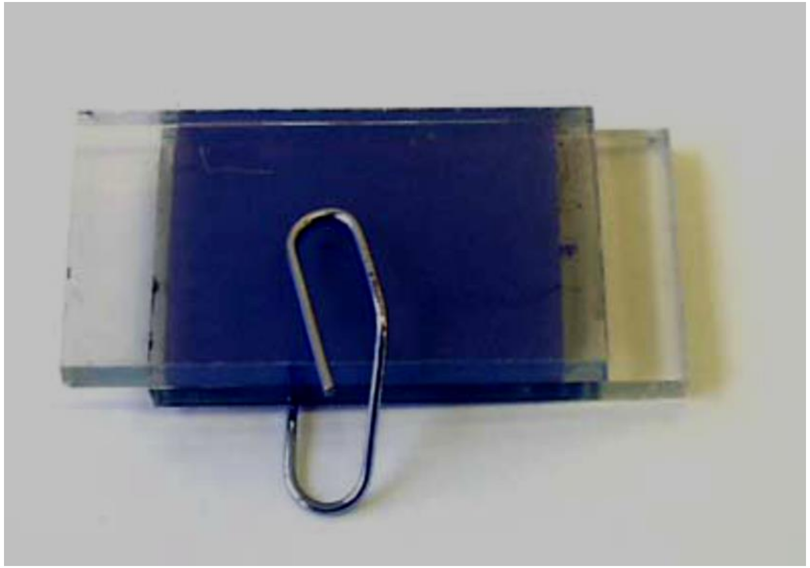

Upper Plate :

Dye coated TiO_2
Plate (Anode)

Lower Plate :

Graphite coated
conductor (Cathode)

Working Principle

The working principle of DSSC involves four basic steps: light absorption, electron injection, transportation of carrier, and collection of current.

- Sunlight energy (photon of light) passes through the titanium dioxide layer and absorbed by the photosensitizer
- Due to the photon absorption, electrons get promoted from the ground state (Dye) to the excited state (Dye*) of the dye
- Excited electrons with a lifetime of nanosecond range are injected into the conduction band of nano-porous TiO_2 electrode which lies below the excited state of the dye.
- As a result, the dye gets oxidized.

$$\mathrm{Dye_o} + h\nu \rightarrow \mathrm{Dye^*}$$

$$\mathrm{Dye^*} \rightarrow \mathrm{Dye^{*+}} + e^- (\mathrm{TiO_2})$$

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),