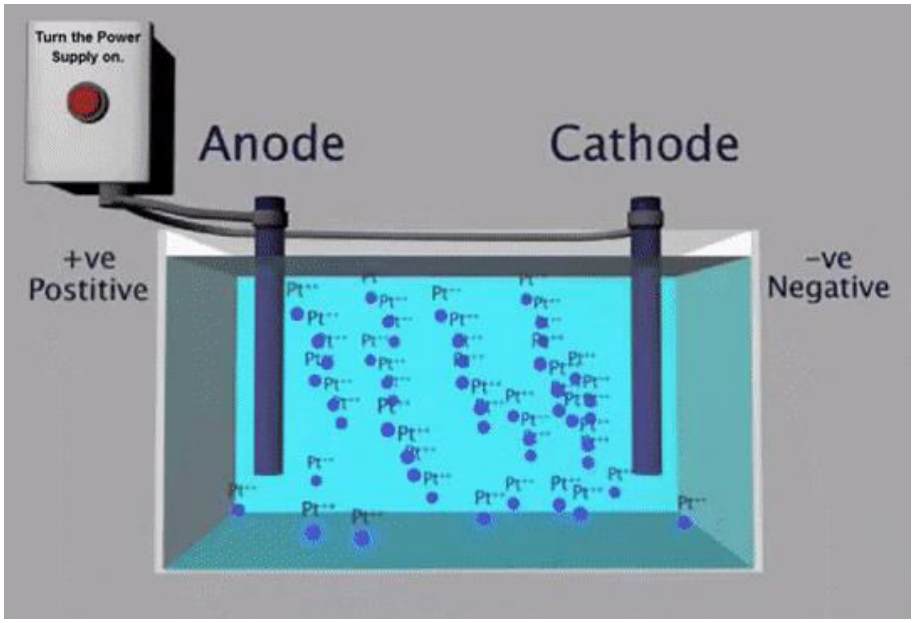
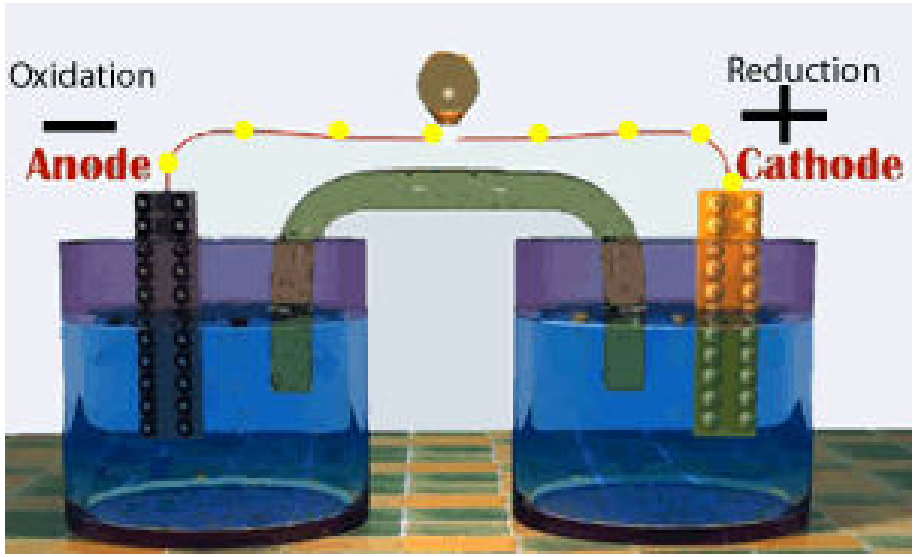
Module – 5: Electrochemical Energy Systems

Brief introduction to conventional primary and secondary batteries; High energy electrochemical energy systems: Lithium batteries – Primary and secondary, its Chemistry, advantages and applications.

Fuel cells – Polymer membrane fuel cells, Solid-oxide fuel cells- working principles, advantages, applications.

Introduction - Electrochemical Cell





Electrolytic Cell

Chemical reaction by passing electric current

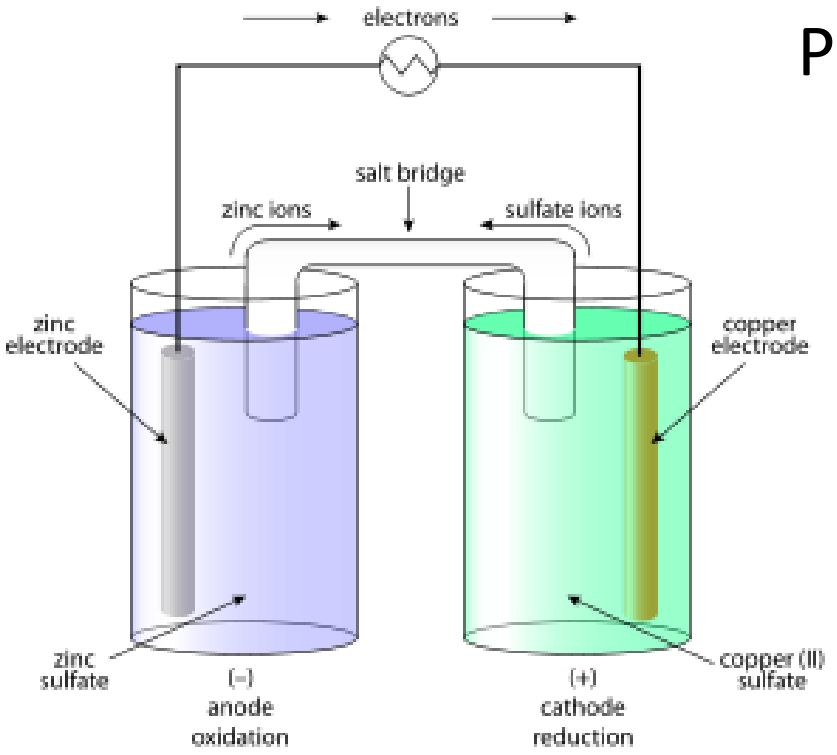
Electrochemical Cell

Chemical redox reaction is utilized to produce electrical current

Electrical energy is converted into chemical energy

Chemical energy is converted into electrical energy

Electrochemical cell



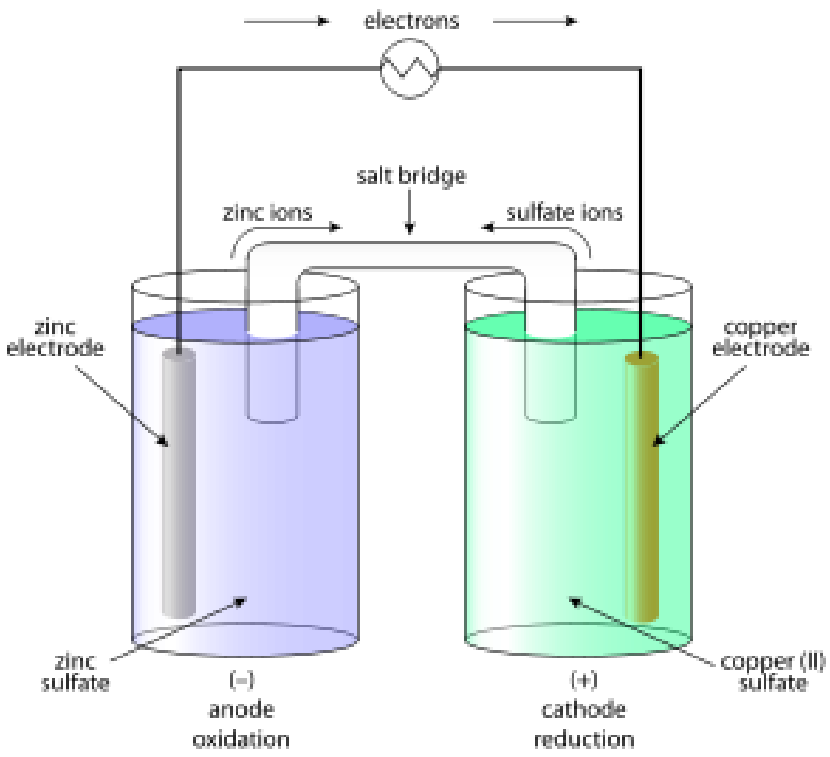
Parts of electrochemical cell

- Electrodes
  - i. Anode
  - ii. Cathode
- Electrolyte
- Separator

Oxidation occurs in Anode

Reduction occurs in Cathode

Electrochemical cell – Daniell cell



Anode

Oxidation

$M \rightarrow M^{n+} + ne^-$ (Loss of electron)

$Zn \rightarrow Zn^{2+} + 2e^-$ (Daniell cell)

Cathode

Reduction

$M^{n+} + ne^- \rightarrow M$ (Gain of electron)

$Cu^{2+} + 2e^- \rightarrow Cu$ (Daniell cell)

Representation of Electrochemical cell

- Anode is written on the left hand side, Cathode is on the write right hand side.

- In the anode side, electrode is written on the left.
  In the cathode side, electrode is written on the right

  Anode electrode | Electrolyte||Electrolyte| Cathode electrode

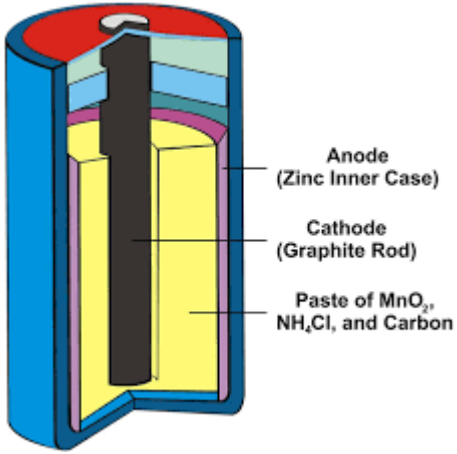
  $Zn \mid Zn^{2+}\ (1M) \mid\mid Cu^{2+}\ (1M) \mid Cu$

- Salt bridge is mentioned as "||"

- Concentration of the electrolyte solution can be mentioned next to the electrolyte

Battery

- A battery is a device consisting of one or more electrochemical cells with external connections provided to power electrical devices.



- An electrochemical cell is a device capable of generating electrical energy from chemical reactions.
  - e.g. Daniell Cell

Types of Battery

- Primary battery (primary cells)
  - In which 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.

- Secondary battery (secondary cells)
  - In which cell reactions **can be reversed** by passing electric current in the opposite direction. Thus it can be used for a large number of cycles.

- Flow battery and Fuel Cell
  - In which materials (reactants, products, electrolytes) pass through the battery, which is simply an electrochemical cell that converts chemical to electrical energy.

Examples

- **Primary batteries**
  i. Dry or lachlanche cell
  ii. Alkaline battery
  iii. Lithium batteries

- **Secondary batteries**
  i. Lead acid
  ii. Nickel-Cadmium
  iii. Nickel Metal hydride
  iv. Lithium ion

- **Flow battery and Fuel Cell**
  i. Polymer Membrane Fuel Cell
  ii. Solid Oxide Fuel Cell

Lithium Primary Cell

- Lithium batteries are different from Lithium ion Batteries (also Known as Li-ion batteries).

- Lithium batteries can not be recharged

- Most of the common lithium batteries contain:

  Anode: **Metallic Li**

  Cathode: **MnO_2**

  Electrolyte**: Li salts dissolved in organic solvents such as Acetonitrile (CH_3CN), propylene carbonate, ethylene carbonate**

Lithium as a Anode Material

The main attractions of lithium as an anode material is

- It is the most electronegative metal in the electrochemical series
- It has very low density, means, the largest amount of electrical energy per unit weight

Lithium Battery

Cell Representation

Li|Li+(non-aqueous)||KOH(paste)|**MnO_2,$Mn(OH)_2$,C**

Anode

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

Cathode

$$Li^+ + MnO_2 + e^- \rightarrow LiMnO_2$$

Overall Reaction

$$Li + MnO_2 \rightarrow LiMnO_2 + Energy$$

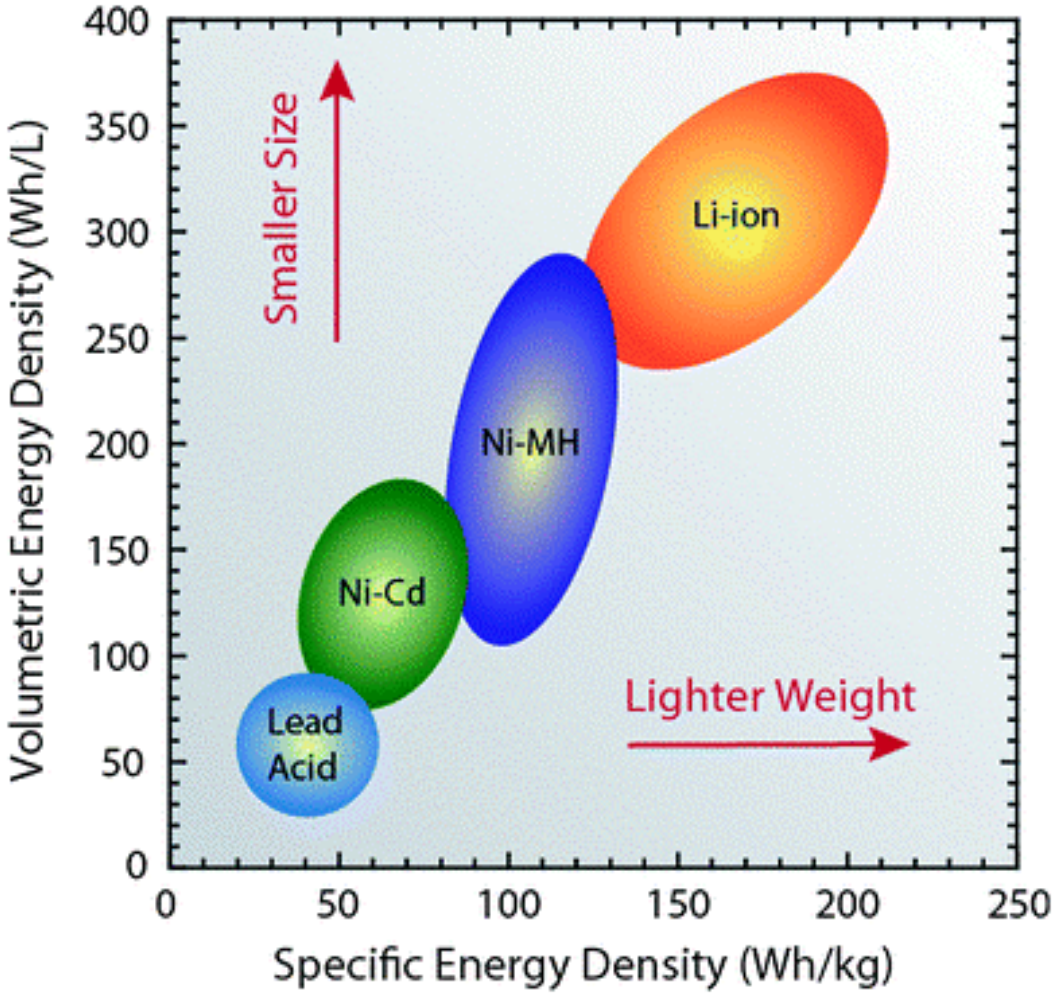
Different types of Lithium Batteries

S. No.	Anode	Cathode	Characteristics	Applications
1	Li	$SOCl_2$	3.6 V, Long Shelf life, Low to Moderate rate applications	Memory Devices, Standby Electrical devices
2	Li	SO_2	3.0 V, Best low temperature performance	Military and Special Industrial needs
3	Li	MnO_2	3.0 V, Small in size, good low temperature performance, low drain applications	Medical Devices, Memory Circuits

Advantages of Lithium battery

- High electron density
- Long shelf life
- Low self discharge
- Need less maintenance
- Can provide very high current

Li-ion battery (Secondary cell)



Nobel Prize in Chemistry 2019

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John B. Goodenough

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M. Stanley Whittingham

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Akira Yoshino

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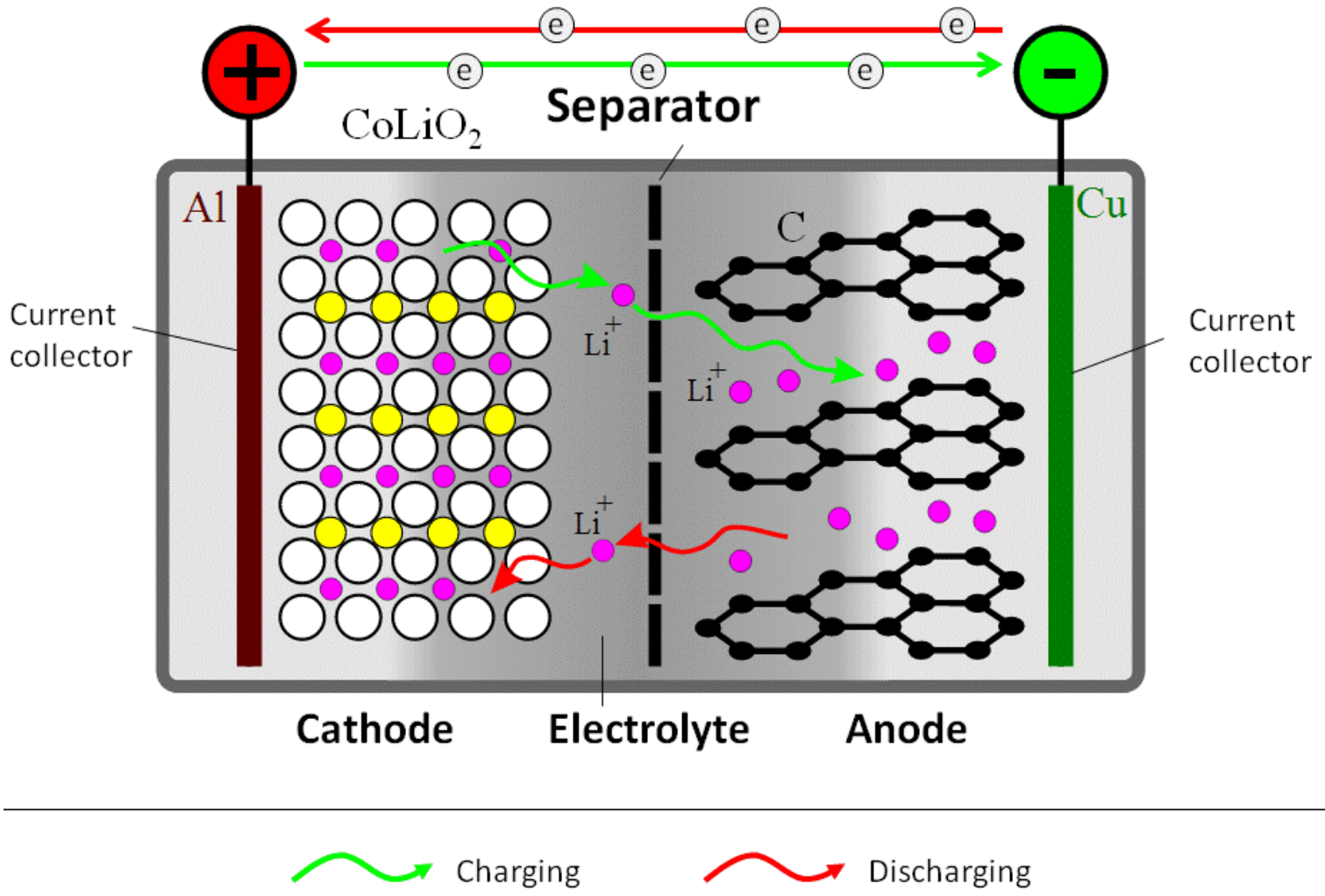
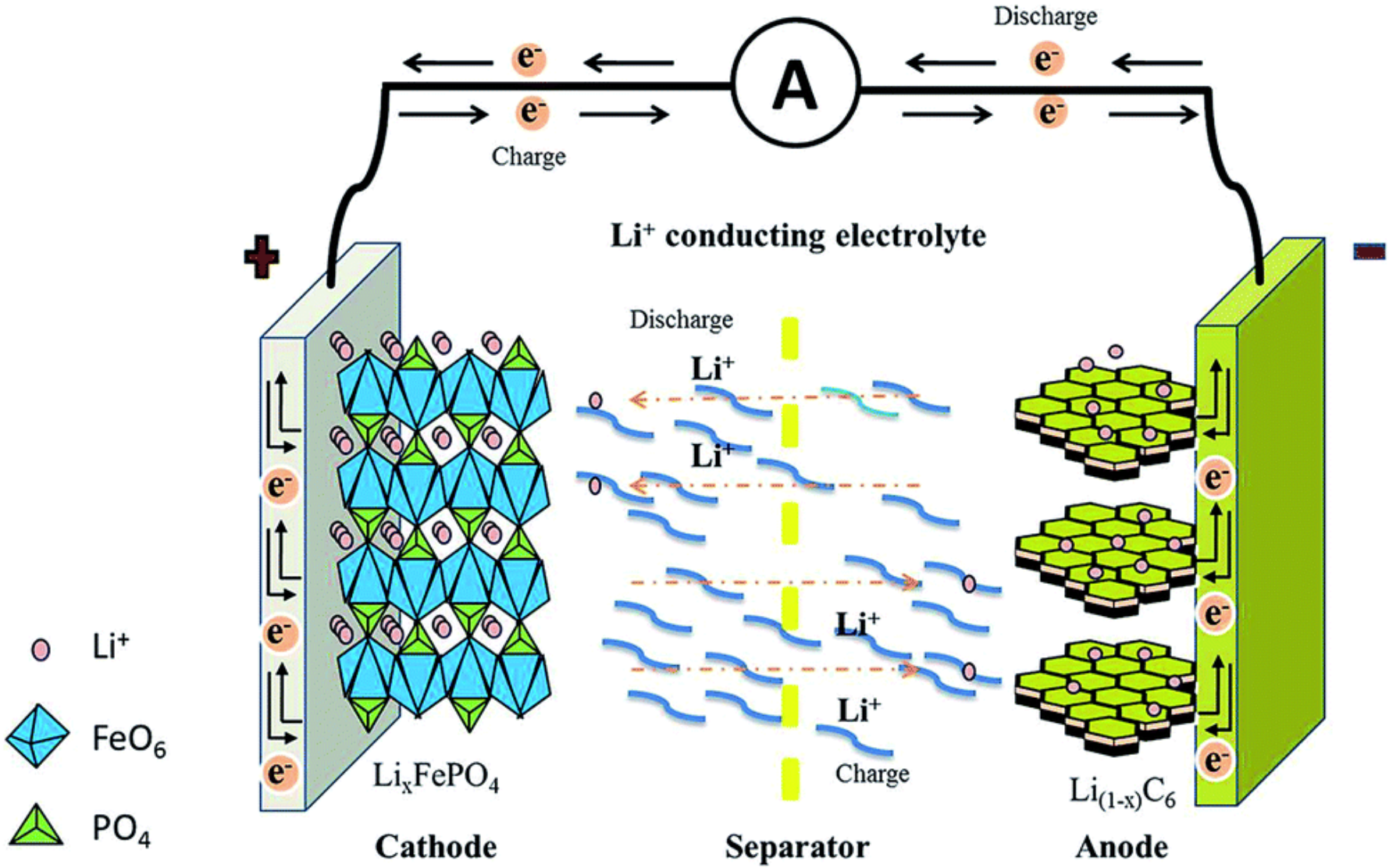
They created a rechargeable world

The Nobel Prize in Chemistry 2019 rewards the development of the lithium-ion battery. This lightweight, rechargeable and powerful battery is now used in everything from mobile phones to laptops and electric vehicles. It can also store significant amounts of energy from solar and wind power, making possible a fossil fuel-free society

Li-ion battery (Secondary battery)



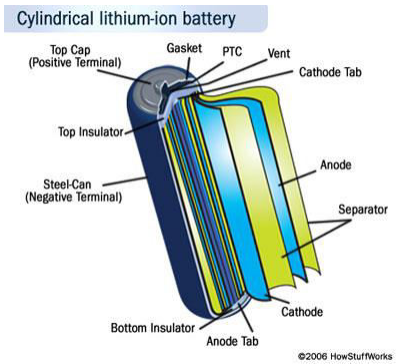
Li-ion battery (Secondary battery)



Lithium ion batteries

Cathode materials

- The most common compounds used for cathode materials are $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$.
- Of these, $LiCoO_2$ has the best performance but is very high in cost, is toxic and has a limited lithium content range over which it is stable.
- $LiNiO_2$ is more stable, however the nickel ions can disorder.
- $LiMn_2O_4$ is generally the best value for money, and is also better for the environment.



Lithium ion batteries

Anodic materials

Sony's original lithium-ion battery used **coke as the anode** (coal product), and since 1997 most Li-ion batteries use **graphite** **to attain a flatter discharge curve**.

Developments also occur on the anode and several additives are being tried, including silicon-based alloys. Silicon achieves a 20 to 30 % increase in specific energy at the cost of lower load currents and reduced cycle life.

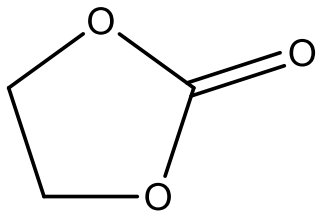
Nano-structured *lithium-titanate* as anode additive shows promising cycle life, good load capabilities, excellent low-temperature performance and superior safety, but the specific energy is low.

Lithium ion batteries

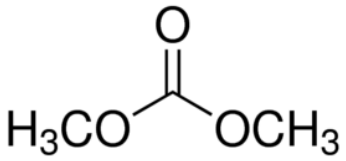
Electrolyte

- Since lithium reacts violently with water, and the cell voltage is so high that water would decompose, a non-aqueous electrolyte must be used.
- A typical electrolyte is $LiPF_6$ dissolved in an ethylene carbonate and dimethyl carbonate mixture.

$LiPF_6$



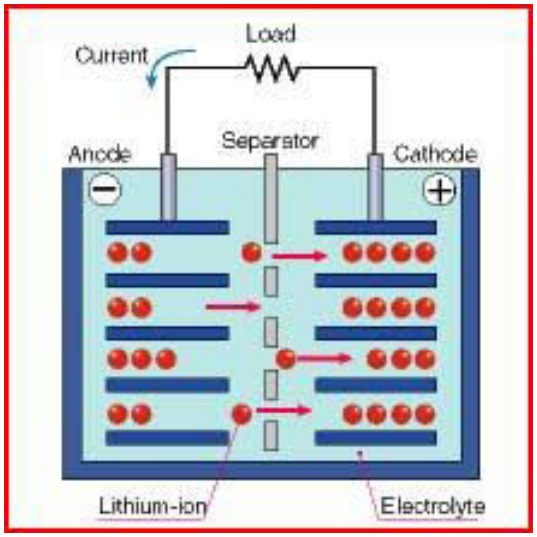
ethylene carbonate



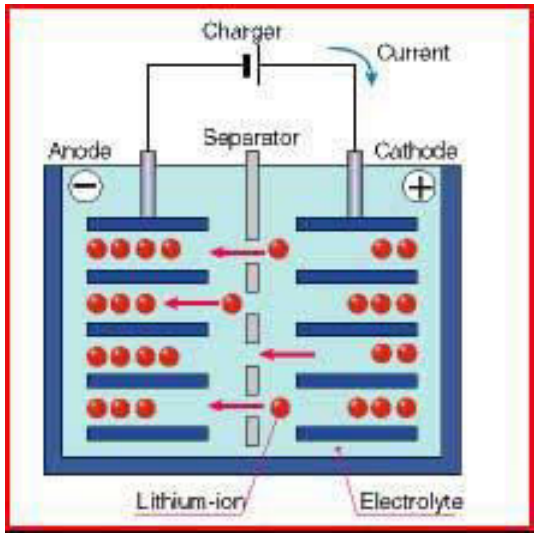
dimethyl carbonate

Lithium ion Cells

Discharging



Charging



Anode: lithium ions in the carbon material

Cathode: lithium ions in the layered material (lithium compound)

Anode

$$Li_{1-X}CoO_2 + C_nLi_x \rightarrow LiCoO_2 + C_n$$

Cathode

$$LiCoO_2 + C_n \rightarrow Li_{1-x}CoO_2 + C_nLix$$

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

Applications: Laptops, cellular phones, electric vehicles

The chemical reactions for charge and discharge are as shown below:

Positive Electrode	$LiCoO_2$	Charge ⇌ Discharge	$Li_{1-x}\ CoO_2 + xLi^+ + xe^-$
Negative Electrode	$C + xLi^+ + xe^-$	Charge ⇌ Discharge	$CLix$
Battery as a Whole	$LiCoO_2 + C$	Charge ⇌ Discharge	$Li_{1-x}\ CoO_2 + CLix$

The principle behind the chemical reaction in the lithium ion battery is one where the lithium in the positive electrode lithium cobalt oxide material is ionized during charge, and moves from layer to layer in the negative electrode. During discharge, the ions move to the positive electrode and return to the original compound

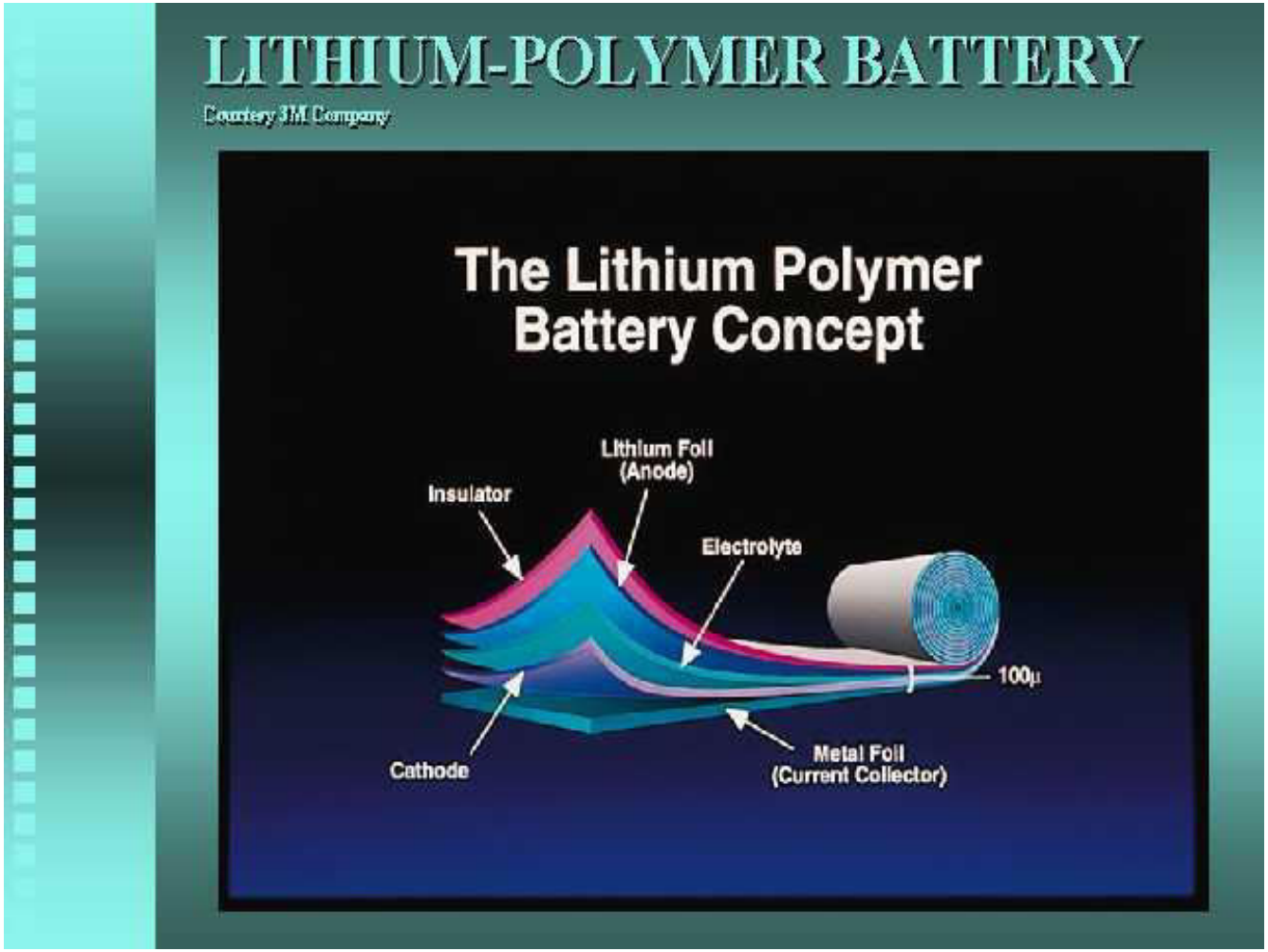
Lithium Polymer batteries are better than Lithium ion batteries

Exploded laptop

- Li-ion batteries use organic solvents to suspend the lithium ions.
- In situations where the structure of the battery is compromised, that solvent can ignite and vent from the pressurized battery.
- The result is a dangerous explosion
- The main advantage of Li-poly batteries is their reluctance to explode under pressure

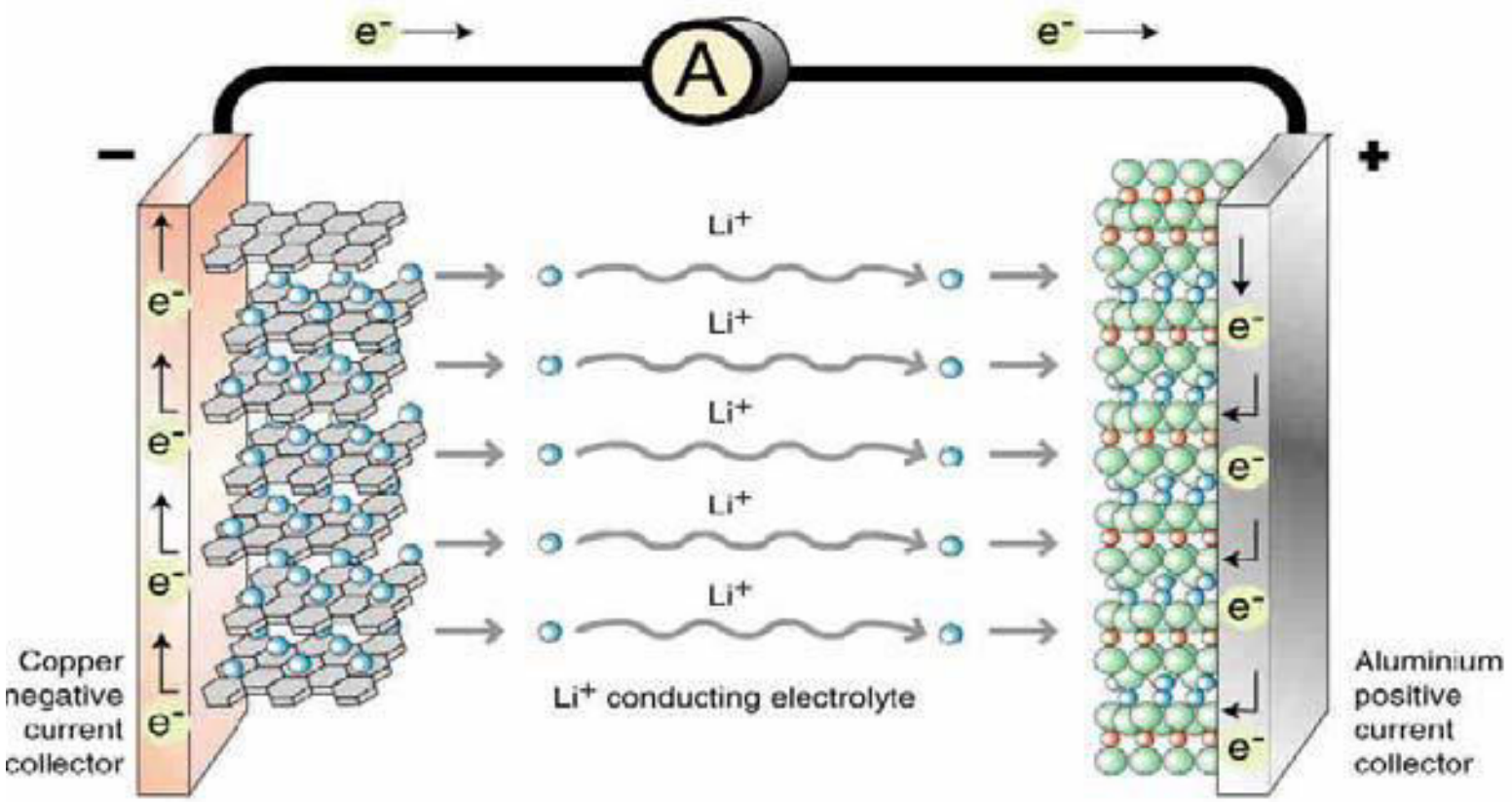
Lithium Polymer Battery

- Electrolyte is a polymer



Lithium polymer (Poly-Carbon Monofluoride) batteries

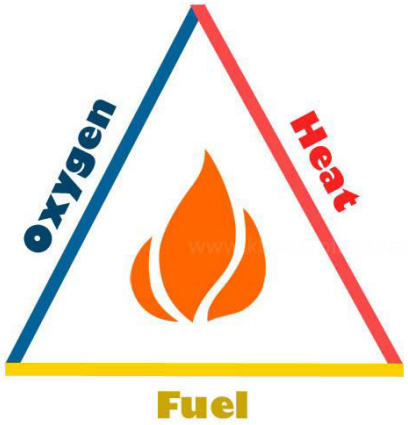
← Charging



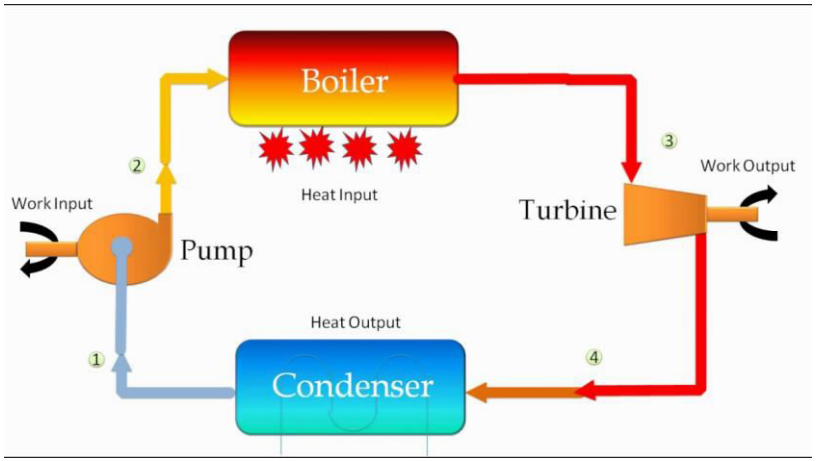
- scientists from Stanford University have found a way to use **silicon nanowires** to produces 10 times the amount of electricity of existing lithium-ion, known as Li-ion, batteries that power laptops, iPods, video cameras, cell phones, and countless other devices. **A laptop that now runs on battery for two hours could operate for 20 hours.**

Fuel – Oxidizer reaction

Combustion



Fire Triangle



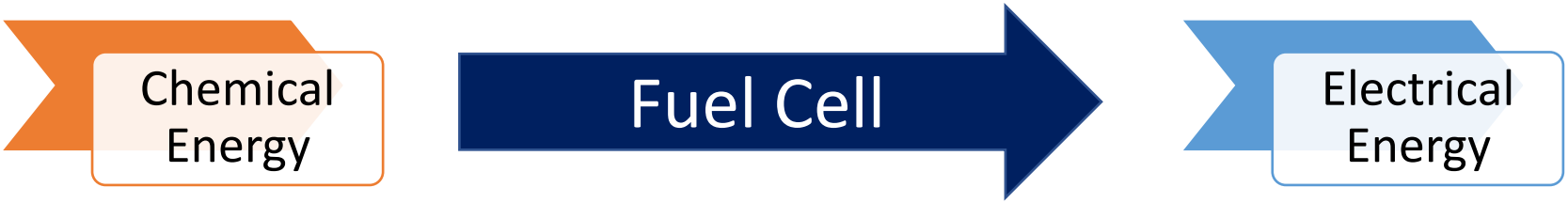
Rankine Cycle

RedOx reaction between Fuel and Oxidizer produces thermal energy → converted in to electrical energy by rankine cycle (Thermal energy → Mechanical energy → Electrical energy)

Fuel Cell

Thermal Power Plants→ Fuel is oxidized to produce thermal energy and it is converted in to mechanical and electrical energy

Fuel cell→ Electrochemical redox reaction of Fuel and Oxidant, directly converts chemical energy in to electrical energy



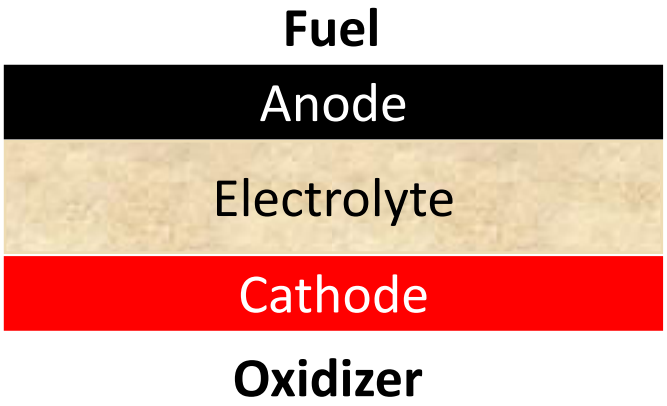
Minimized Interconversion Loss →

Efficient

Fuel Cell

- Electrochemical Cell having a separate fuel-oxidizer system that produces electrical energy by oxidation of Fuel at Anode and the reduction of Oxidizer at Cathode.
- Fuel and Oxidizer are stored outside the battery and supplied as needed.
- Supply of Fuel and Oxidizer → Production of electricity
- High efficiency and Pollution free
- By products are Water and Heat
- Used in NASA Apollo Space Crafts
- e.g. H_2-O_2 Fuel Cell, Solid Oxide Fuel Cell

Fuel Cell Components



- Fuel
- Oxidizer
- Electrodes
  - Anode – Catalyze the oxidation of fuel
  - Cathode – Catalyze the reduction of Oxygen
- Electrolyte
  - Only allows Ions to pass through and blocks electron flow

Fuel / Electrode // Electrolyte // Electrode / Oxidizer

$H_2 - O_2$ Fuel Cell

- Electrolysis of water → Splitting of water produces H_2 and O_2.

(Electrolytic cell)

Sir William Grove
(invented - 1839)

Reverse reaction ??

- Combining H_2 and O_2 to produce H_2O

(Electrochemical Cell)

- Gas Voltaic Battery

Fuel Cell Types

- Based on Electrolyte
  - Alkaline Fuel Cell – **KOH**
  - Polymer Membrane Fuel Cell – Polymer electrolyte – **Nafion**
  - Solid Oxide Fuel cell – Oxide electrolyte – Y doped Thoria, Ceria Stabilize Zirconia

Type of Fuel Cell	Electrolyte type	Electrolyte Example	Ions transported	Water formation in
Alkaline	Alkaline	KOH	OH^-	Anode
Polymer Membrane	Proton conducting Polymer	Nafion	H^+	Cathode
Solid Oxide fuel cell	Metal oxide	Y-doped Thoria	O^{2-}	Anode

Alkaline Fuel cell (or) $H_2 - O_2$ Fuel Cell

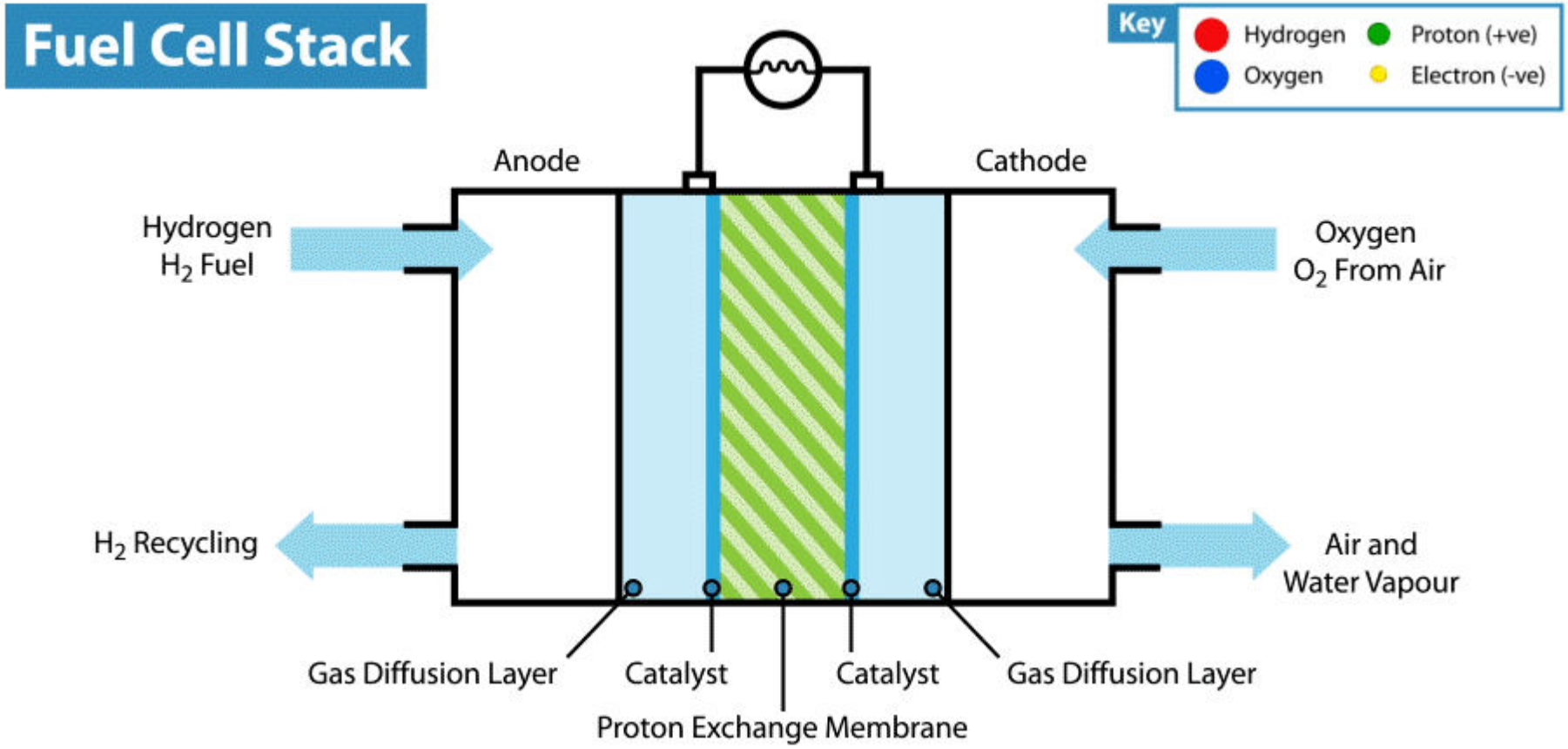
- Fuel – Hydrogen
- Oxidizer – Oxygen
- Electrodes

  Anode – Pt (or) Pd electrode

  Cathode – Pt (or) Ag
- Electrolyte

  KOH

$H_2 - O_2$ Fuel Cell



$H_2 - O_2$ Fuel Cell Reactions

- Anodic reaction

$$2H_2 + 4OH^- \rightarrow 2H_2O + 4e^-$$

- Cathodic Reaction

$$O_2 + 4H_2O + 4e^- \rightarrow 4\ OH^-$$

Net Reaction

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

Requirements for Good Fuel Cell

- Electrodes should catalyze the anodic and cathodic reactions
- Fuels should be Pure and Cheap - Hydrogen!!
- Oxidizers used Oxygen or Air → Pure oxygen is preferred

Limitations of Fuel Cell

- Pure Hydrogen…
- Electrode and electrolyte contamination/degradation
- Cost of Catalyst – Pt and Pd !!!
- Safety!!

High temperature → Improved kinetics, low risk of contamination

Materials stable at high temperature is needed

Solid Oxide Fuel Cell (SOFC)

29\Fuel Cell_Module_5_(III)

Types of Fuel Cell

Based on the operational temperature

- Low Temperature Fuel Cell – Fuel – Pure Hydrogen (below 100 ^{o}C)
- Mid Temperature Fuel Cell – Fuel – Hydrogen or Reformed Hydrocarbons (100-300 ^{o}C)
- High Temperature Fuel Cell – Fuel – Hydrocarbons, Electrolytes – solid ceramics (~1000 ^{o}C)

Solid Oxide Fuel Cell

- $H_2 – O_2$ Fuel Cell

  H_2 → H^+ diffuses through electrolyte to cathode

- Solid Oxide Fuel Cell

  O_2 → $2O^{2-}$ diffuses through electrolyte to anode

Electrolyte → Good oxide ion conductor and poor electron conductor

- Operates at high temperature so diffusion rate is higher.
- Electrical insulating oxide with non-stoichiometry

e.g. Yttria Stabilized Zirconia (YSZ), Gadolinium Doped Ceria (GDC)

Solid Oxide Fuel Cell (SOFC)

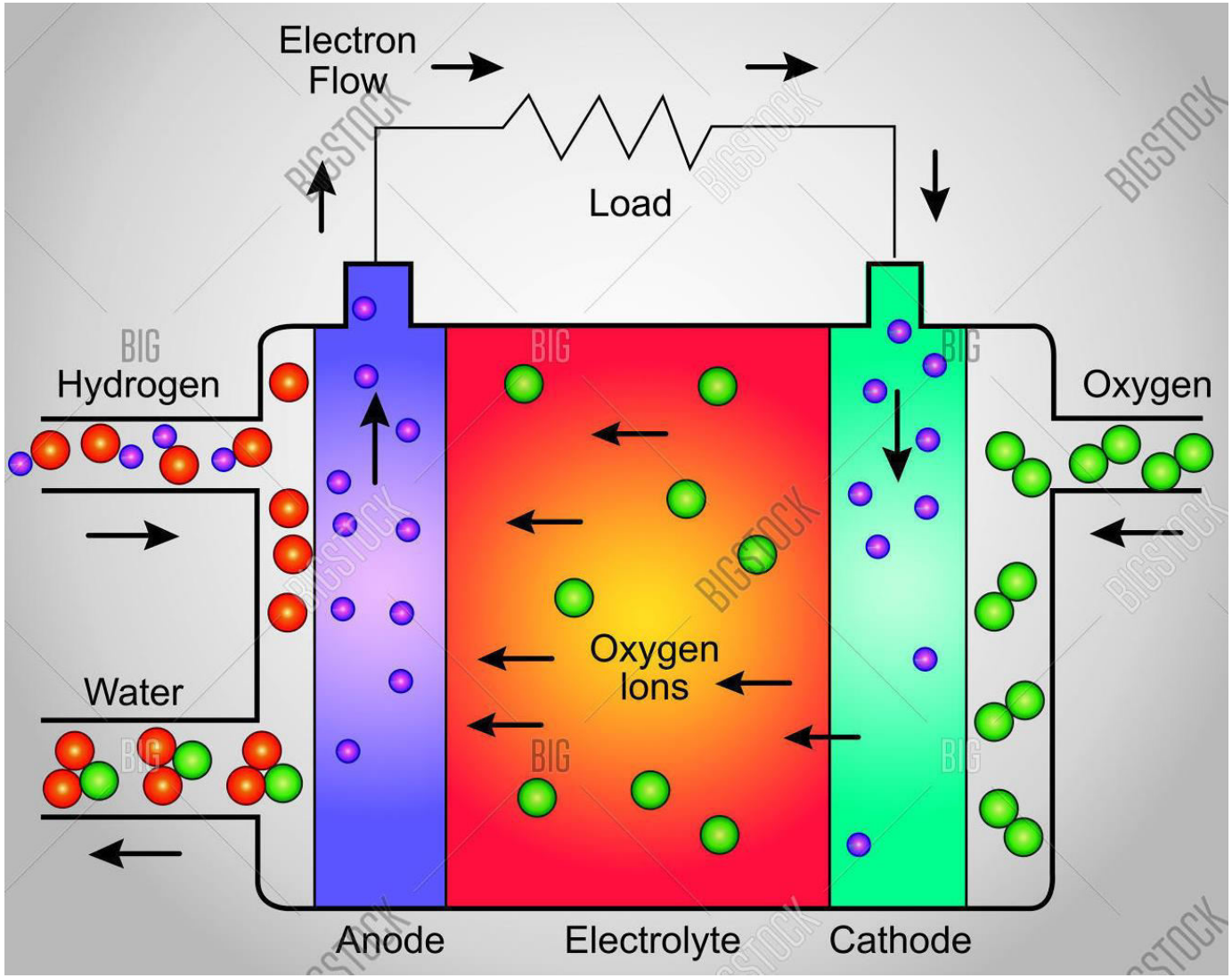
- Fuel – Hydrogen
- Oxidizer – Oxygen
- Electrodes

  Anode – Mixture of Ni and Yttria Stabilized Zirconia (YSZ)

  Cathode – Sr-doped Lanthanum Manganite ($La_{1-x}Sr_xMnO_3$)
- Electrolyte

  Oxide ion conductors (YSZ, GDC)

Solid Oxide Fuel Cell



Solid Oxide Fuel Cells - Reactions

- Anode reaction

$$2H_2+2O^{2-} \rightarrow 2H_2O + 4e^-$$

- Cathode Reaction

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

- Net reaction

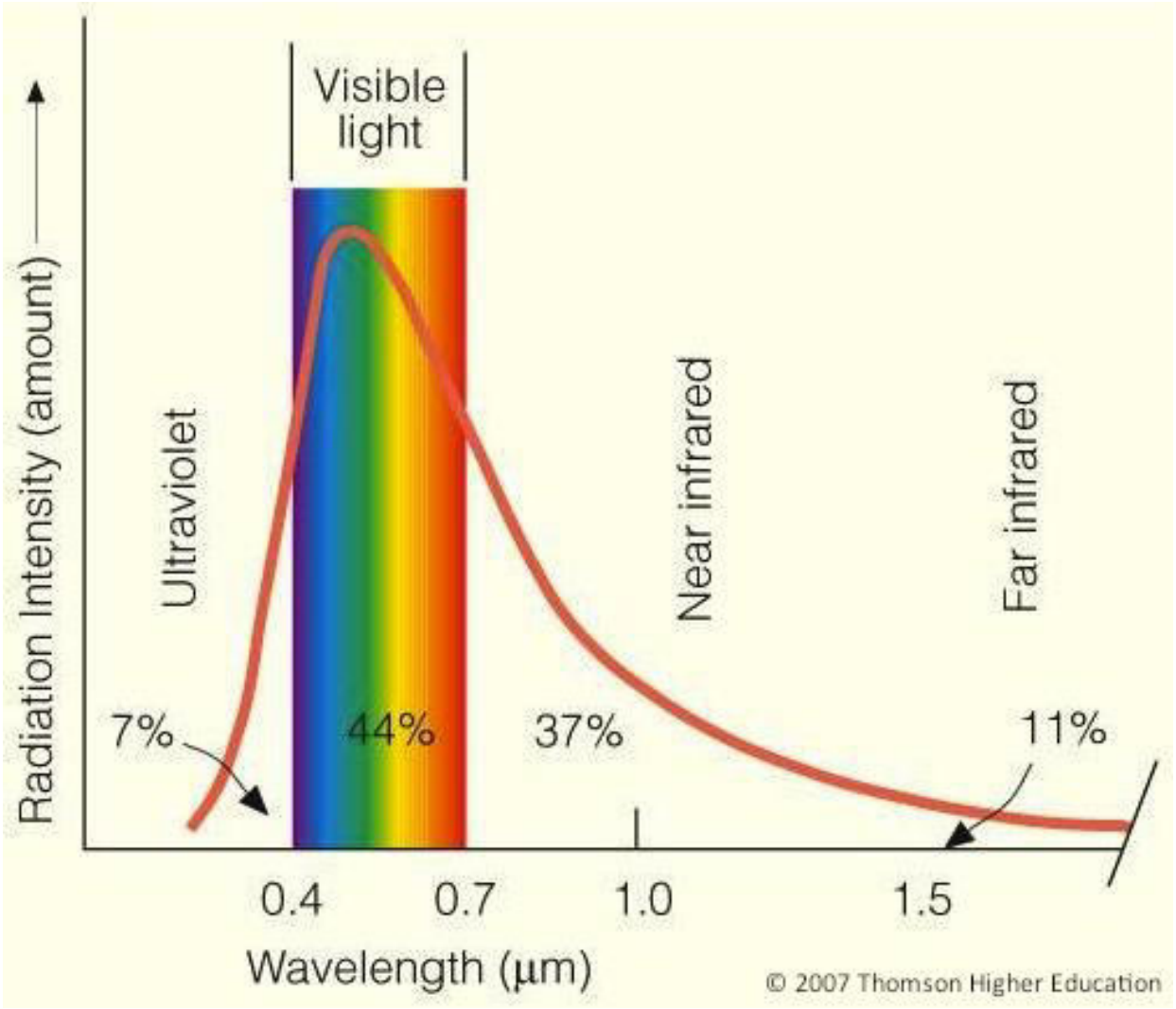
$$2H_2 + O_2 \rightarrow 2H_2O$$

In $H_2 – O_2$ fuel cell water is formed on cathode side
In SOFC water is formed on anode side.

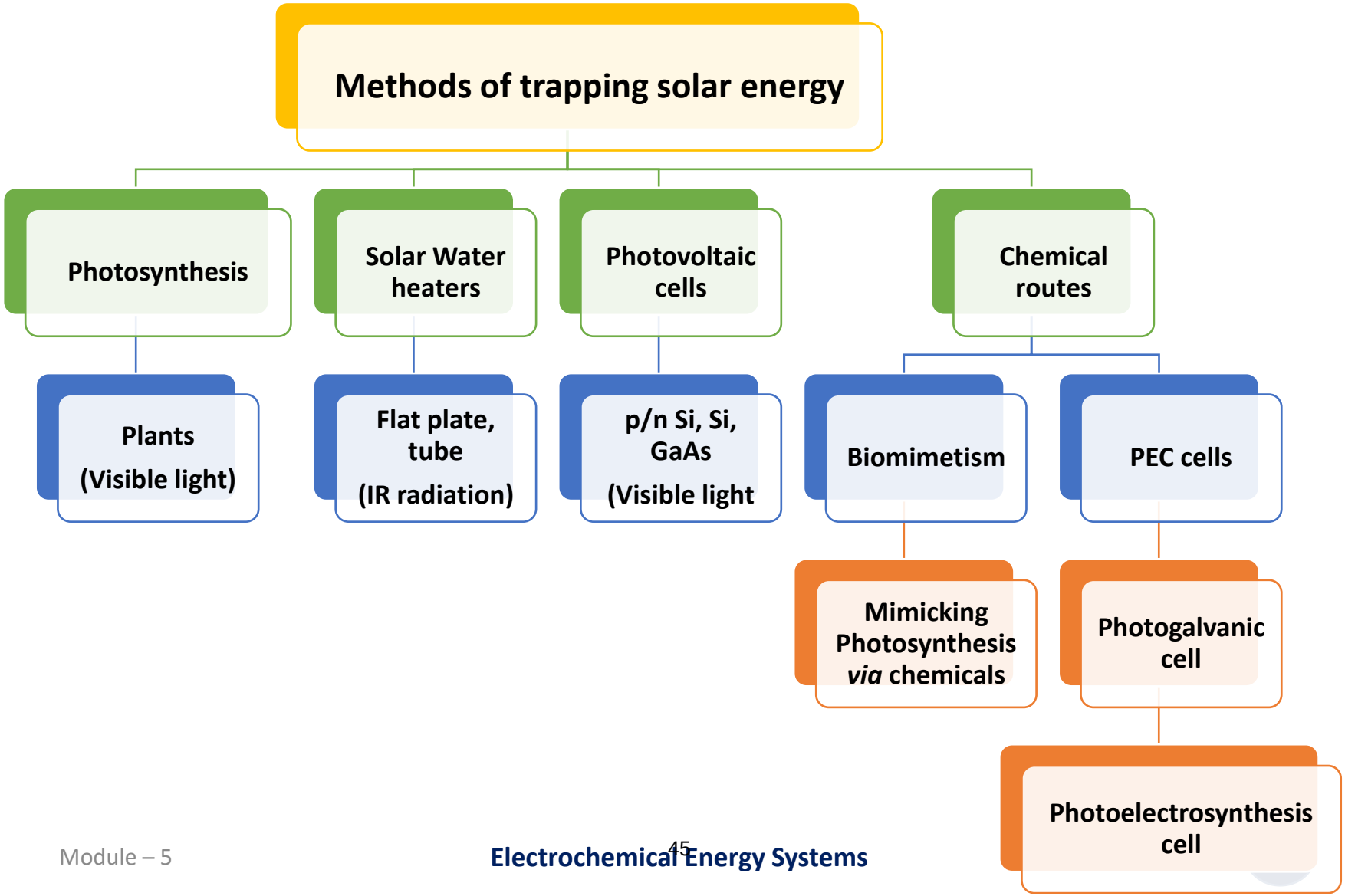
Advantages of Fuel Cell

- Low maintenance cost
- Silent operation
- Produces pure water as a product
- Heat generated during H_2O formation can also be used
- High energy conversion efficiency
- They can be used as auxiliary power units

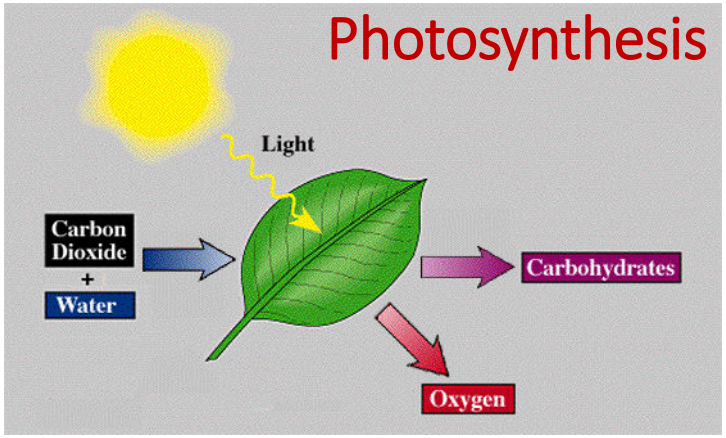
Spectral Properties of Sunlight



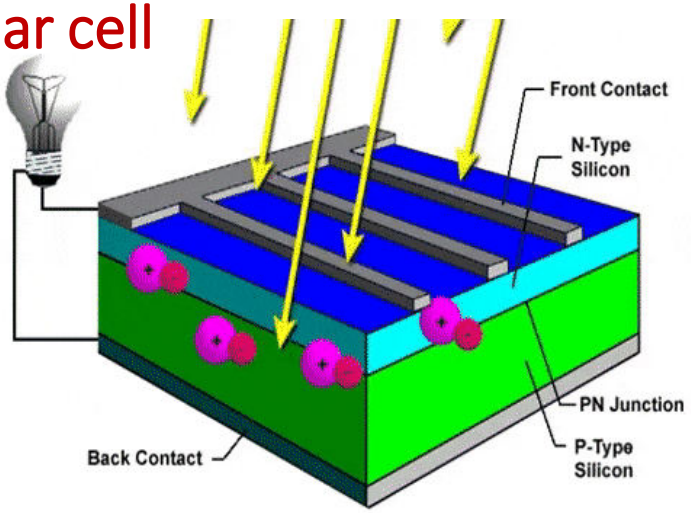
Solar energy conversion devices



Solar Energy Conversion

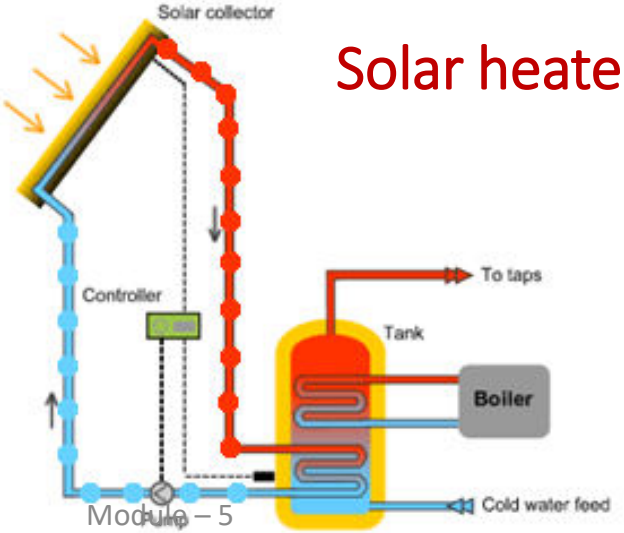


Solar cell



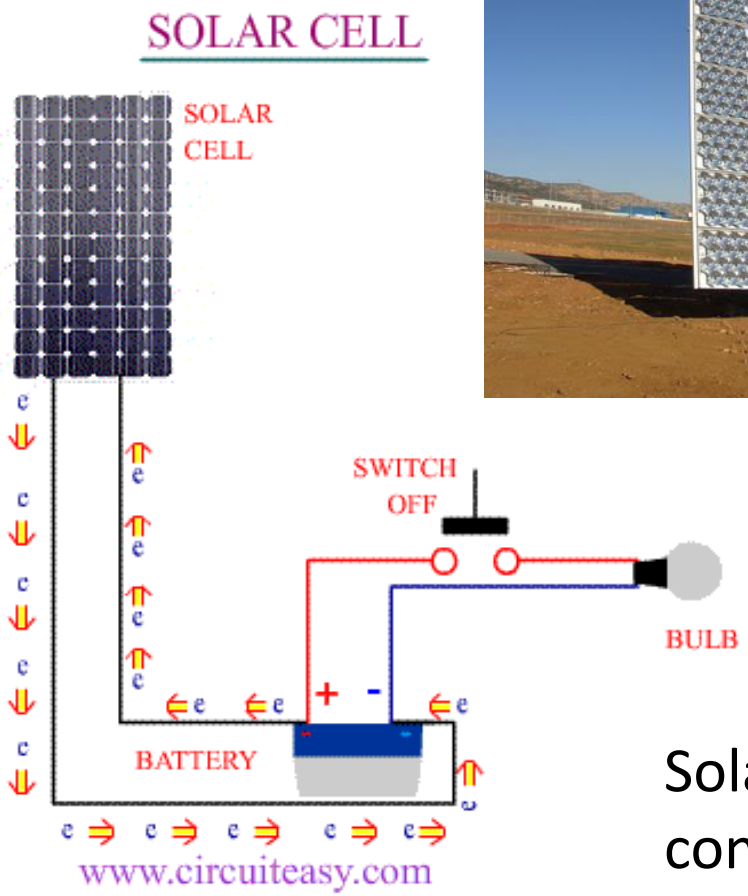
Solar Energy Conversion

Solar heater



Solar cell

PHOTON



Solar cell is a device that directly converts the **energy of light** into **electrical energy**

Types of solar energy conversion cells

(1) Photovoltaic Cells

- Photovoltaic cell, is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect

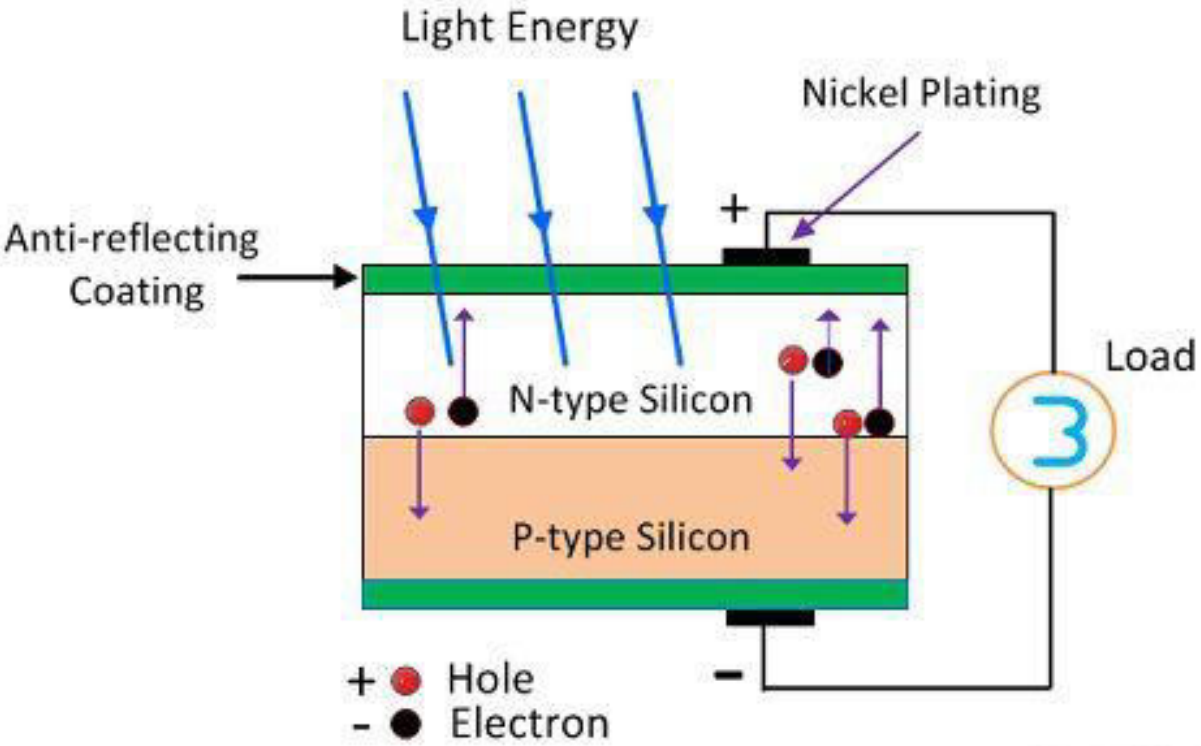
(2) Photoelectrochemical cells

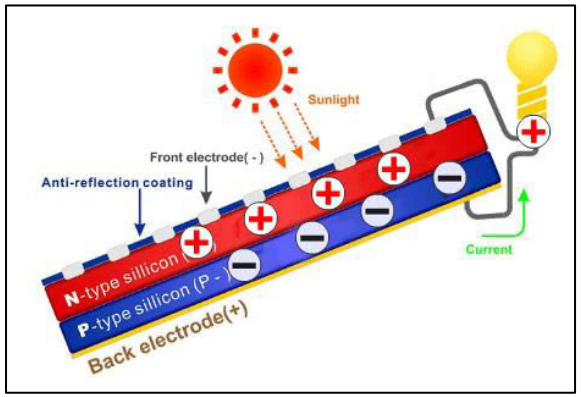
- Photoelectrochemical cell is a photocurrent-generated device composed of an electrolyte, a photoactive semiconductor electrode

(3) Dye-sensitized solar cells

- Dye-sensitized solar cells (DSC) is a photoelectrochemical solar cell, consisting of a dye-sensitized semiconducting working electrode (WE), a redox electrolyte and a counter electrode (CE)

(1) Photovoltaic Cells



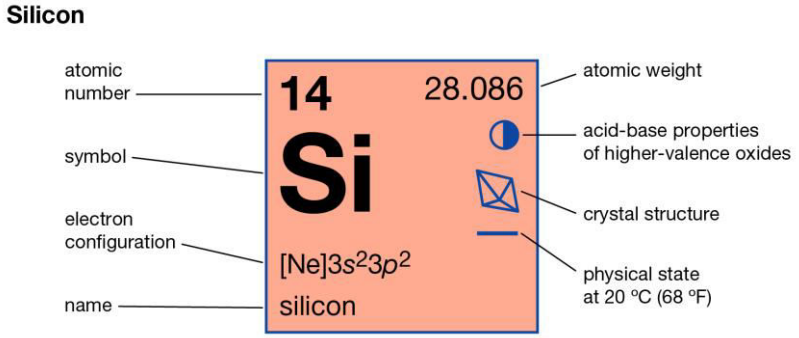


- **System converts light energy to electricity**
- **Applications in Aerospace & Satellite etc.**

Photovoltaic Cells

- A photovoltaic 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.
- In the photoelectric effect electrons are ejected from a material's surface upon exposure to radiation of sufficient energy.

Why Silicon?

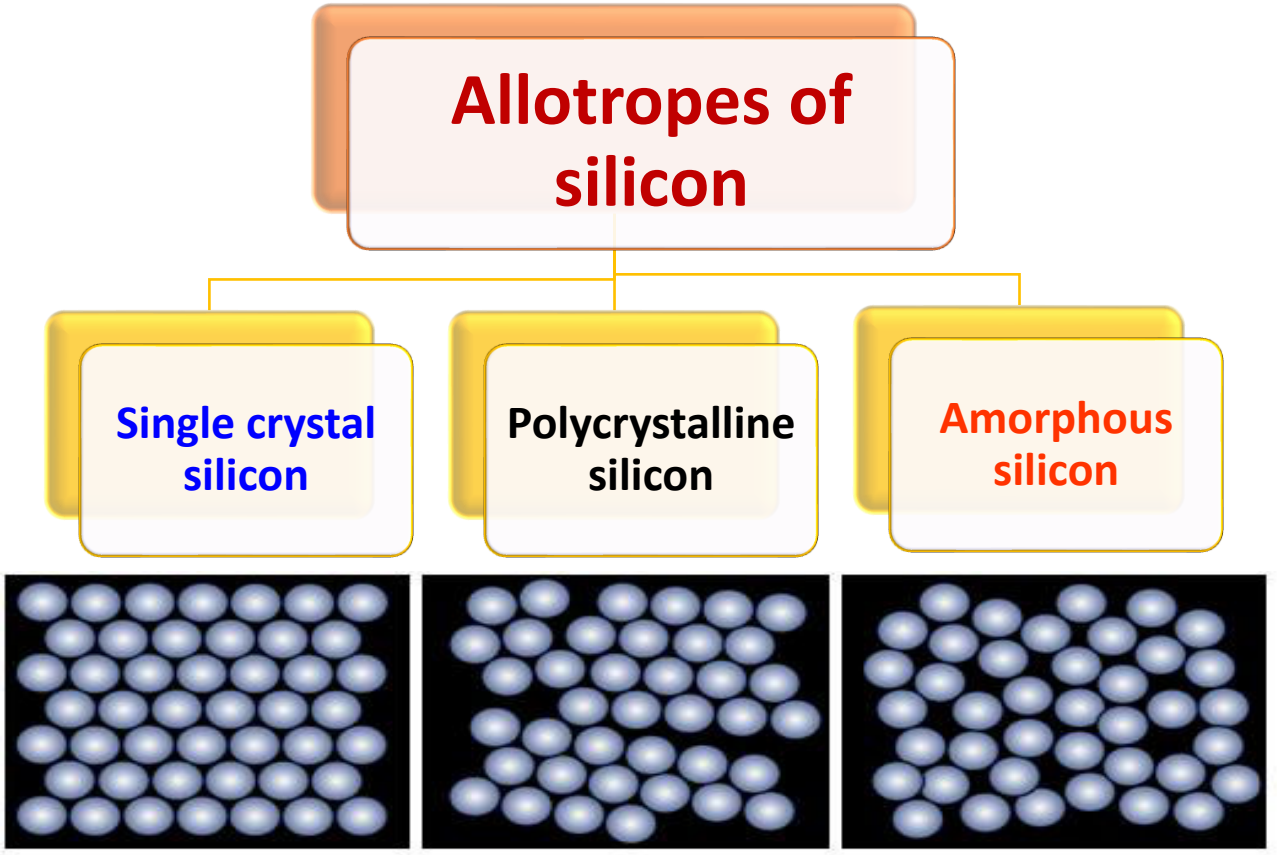


- Silicon is a very common element abundant in nature. It is the main element in sand and quartz.
- Silicon is considered as the most suitable material for solar energy conversion because of

1) Most abundance (~28% by mass) after oxygen
2) Optimum band gap of 1.23 eV at 300 K
3) Cost effectiveness
4) Interestingly, silicon has a greater density in a liquid state than a solid state.

Structure of Silicon

The crystal structure, or atomic arrangement, of any material has a great deal to do with its electrical properties.



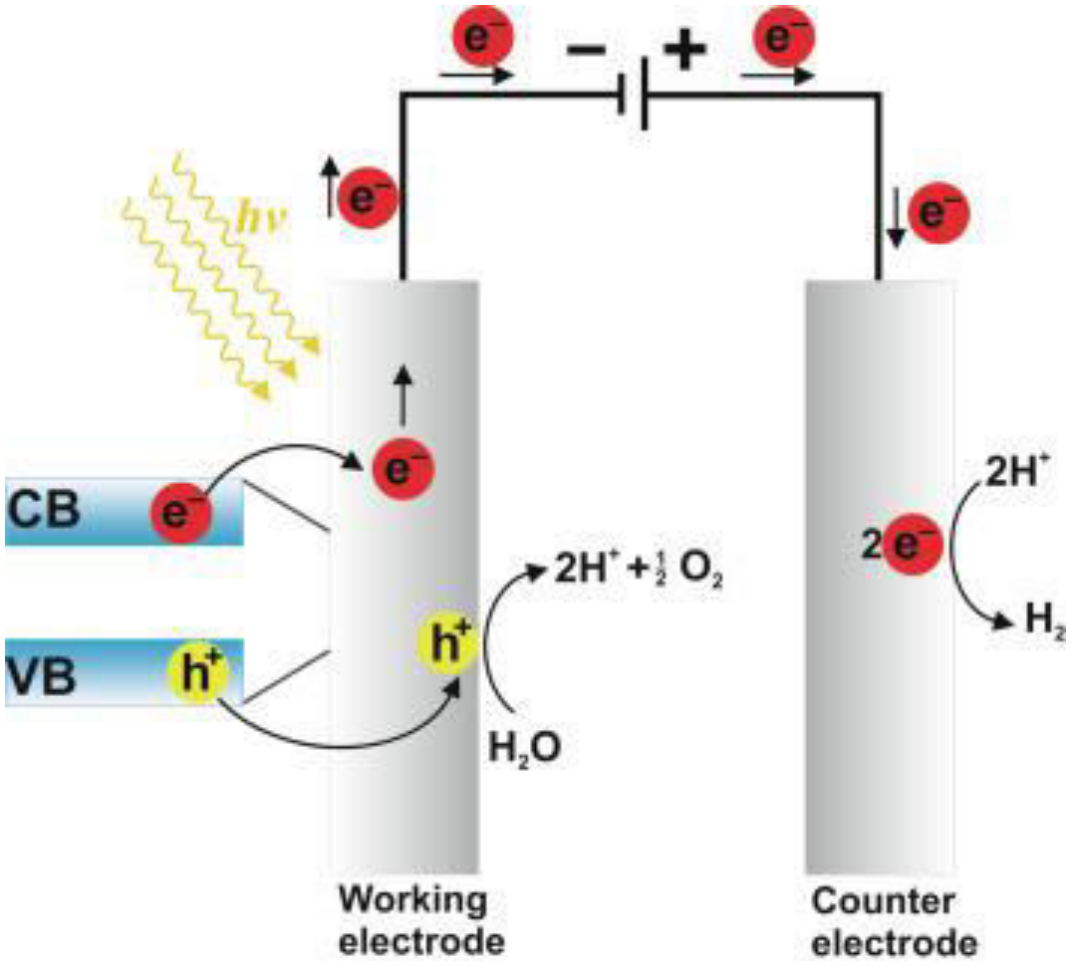
Types of silicon

- **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.

- **Polycrystalline 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.

- **Amorphous silicon (non-crystalline for higher light absorption) -** The final category, the amorphous material, displays no atomic regularity of arrangement on any macroscopic scale.

(2) Photoelectrochemical cells



Types of Photoelectrochemical cells

Photo-electrochemical cells are classified into two types according to their application

1. Liquid Junction Solar Cell (LJSC) –
   - This cell is used to convert solar energy into electrical energy

2. Photo-electrosynthesis (PES) cells –
   - In this class of cells, solar energy is converted into chemical energy in the form of fuels.

Conditions for Efficient Solar Energy Conversion – Electrodes

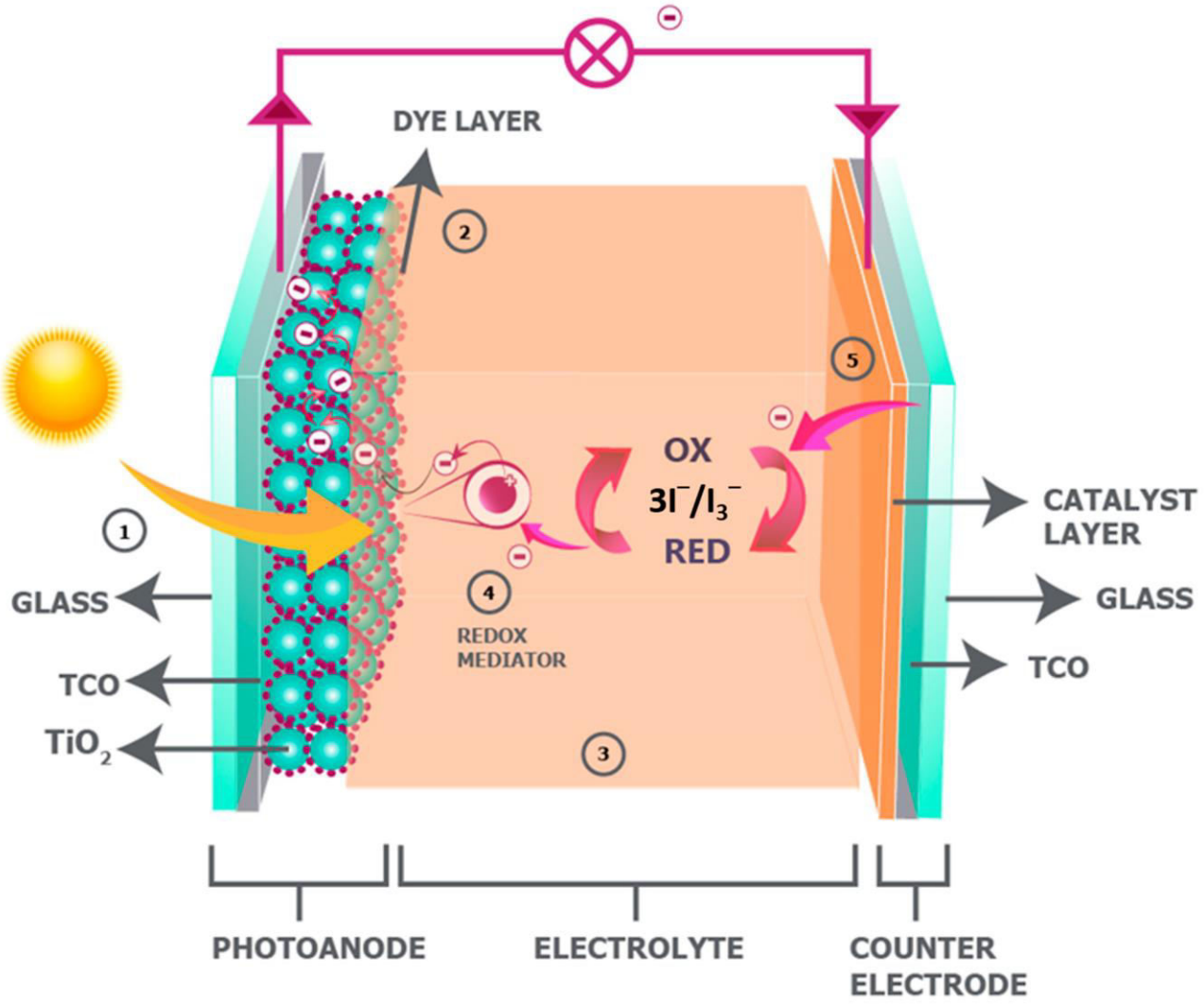
The requirements for the electrode materials are:

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.

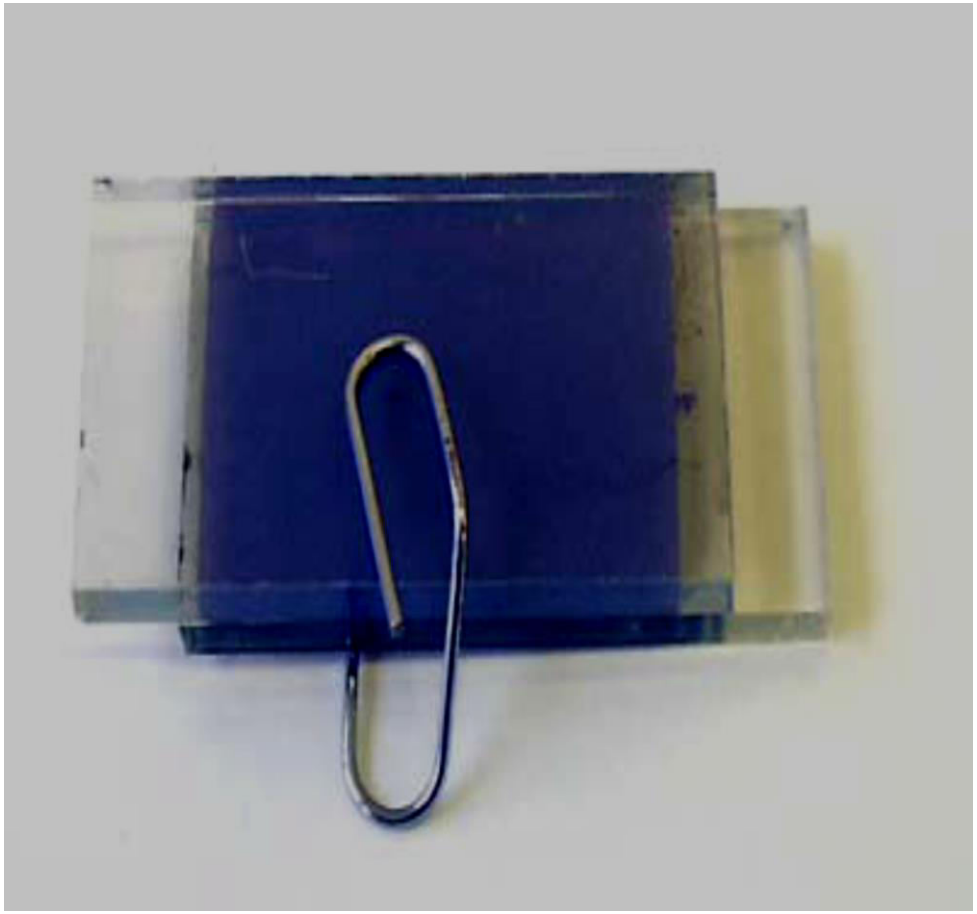
(3) Dye-sensitized solar cells - Grätzel cell



Dye-sensitized solar cells - 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 oxidized (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.

Dye-sensitized solar cells - Grätzel cell



Prepared Grätzel cell

Upper Plate :

Dye coated TiO_2 Plate (-Ve)

Lower Plate :

Graphite coated conductor (+Ve)

By Hermetic sealing

Applications of solar cell

Solar cells are used in a wide variety of applications

- Toys, watches, calculators
- Electric fences
- Remote lighting systems
- Water pumping
- Water treatment
- Emergency power
- Portable power supplies
- Satillites

Module – 6: Fuels and Combustion

- Calorific value - Definition of LCV, HCV. Measurement of calorific value using bomb calorimeter and Boy's calorimeter including numerical problems.
- Controlled combustion of fuels - Air fuel ratio - minimum quantity of air by volume and by weight - Numerical problems
- Three way catalytic converter - selective catalytic reduction of NO_X
- Knocking in IC engines - Octane and Cetane number - Anti-knocking agents.

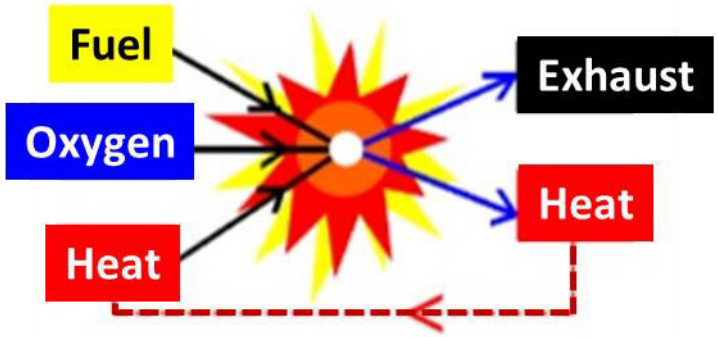
Fuel

- **Fuel:** Anything which burn to give heat in presence of oxygen

$$\text{Fuel} + O_2 \rightarrow \text{Product} + \text{Heat}$$

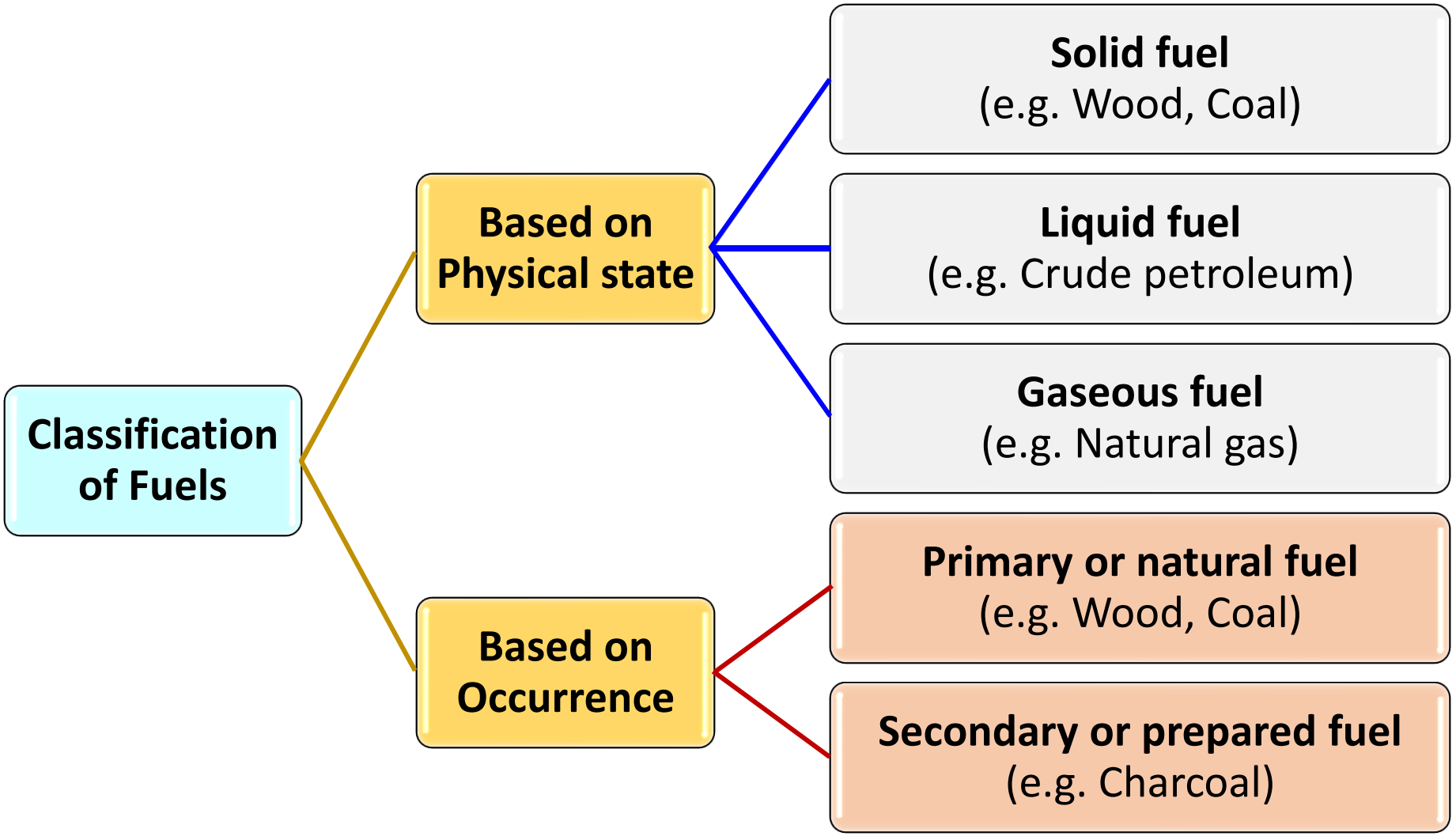
- **Combustion:** The process of burning fuel. In other words, combustion involves oxidation of fuels to CO_2 and H_2O.

$$H_2 + O_2 \rightarrow H_2O + \text{Heat}$$
$$C + O_2 \rightarrow CO_2 + \text{Heat}$$
$$CH_4 + O_2 \rightarrow CO_2 + H_2O + \text{Heat}$$



- During this fuel combustion process large amount of heat energy is liberated which can be utilized.

Classification of Fuel



Characteristic of good fuel

1. It should **ignite easily**
2. It should give out a **lot of heat (High calorific value)**
3. It should have **low smoke** and **low combustible matter** such as ash
4. It should be **inexpensive** and **readily available**
5. It should be **easy to store and transport**
6. It should have **low ash content**

Calorific value of fuels

- **Calorific value:** The total quantity of heat liberated when a unit mass or volume of the fuel is burnt completely **(capacity to supply heat)**.

- **Units:** cal/g (or) kJ/kg.

- **Calorie:** The amount of heat required to raise the temperature of one gram of water through one degree centigrade.

Fuel	Calorific Value (kJ/kg)
Cow dung cake	6000-8000
Wood	17000-22000
Coal	25000-33000
Petrol	45000
Kerosene	45000
Diesel	45000
Methane	50000
CNG	50000
LPG	55000
Biogas	35000-40000
Hydrogen	150000

Calorific Value = Heat produced on burning of 1 kg of fuel

Types of calorific value

Calorific value

- **Higher or Gross Calorific Value**
  - HCV or GCV
- **Lower or Net Calorific Value**
  - LCV or NCV

Determination of Calorific Value

- **Bomb Calorimeter**
  - HCV (or) GCV
- **Boy's Calorimeter**
  - Gaseous (or) Liquid fuels

Higher or Gross Calorific Value (HCV or GCV)

It is defined as

The total amount of heat liberated, when a unit mass of fuel is burnt completely and the products of the combustion are cooled down to room temperature

- Usually, all fuels contain some hydrogen
- When the calorific value of hydrogen containing fuel is determined experimentally, the hydrogen is converted to steam.
- If the products of combustion are condensed to room temperature (25°C), the steam gets condensed into water and latent heat is evolved.
- The latent heat of condensation of steam also gets included in the measured heat.
- A good fuel posses HCV

Lower or Net Calorific Value

It is defined as

The net heat produced when unit mass / volume of the fuel is burnt completely and the products are permitted to escape

- In actual use of fuel, the water vapour and moisture *etc.* are not condensed and escapes as such along with hot combustion gases. Hence a lesser amount of heat is available.
- Net or lower calorific value can be found from GCV value

NCV = GCV - Latent heat of water vapour formed

= GCV - Mass of hydrogen x 9 x latent heat of steam

- 1 part by mass of hydrogen produces 9 parts by mass of water. The latent heat of steam is 587 kcal/kg formed at room temperature. (i.e. 25°C).

Latent heat of water vapour formed

Latent heat of water vapours is 587 kcal/kg

Hydrogen in the fuel reacts with oxygen to give water

$$H_2 + 1/2\,O_2 \rightarrow H_2O$$

$$2H = 1/2O_2 = H_2O$$

$$2\text{parts} = 16\text{parts} = 18\text{parts}$$

$$1\text{parts} = 8\text{parts} = 9\text{parts}$$

Thus,

$$\mathbf{NCV = GCV - 0.09H * 587}$$

Note:

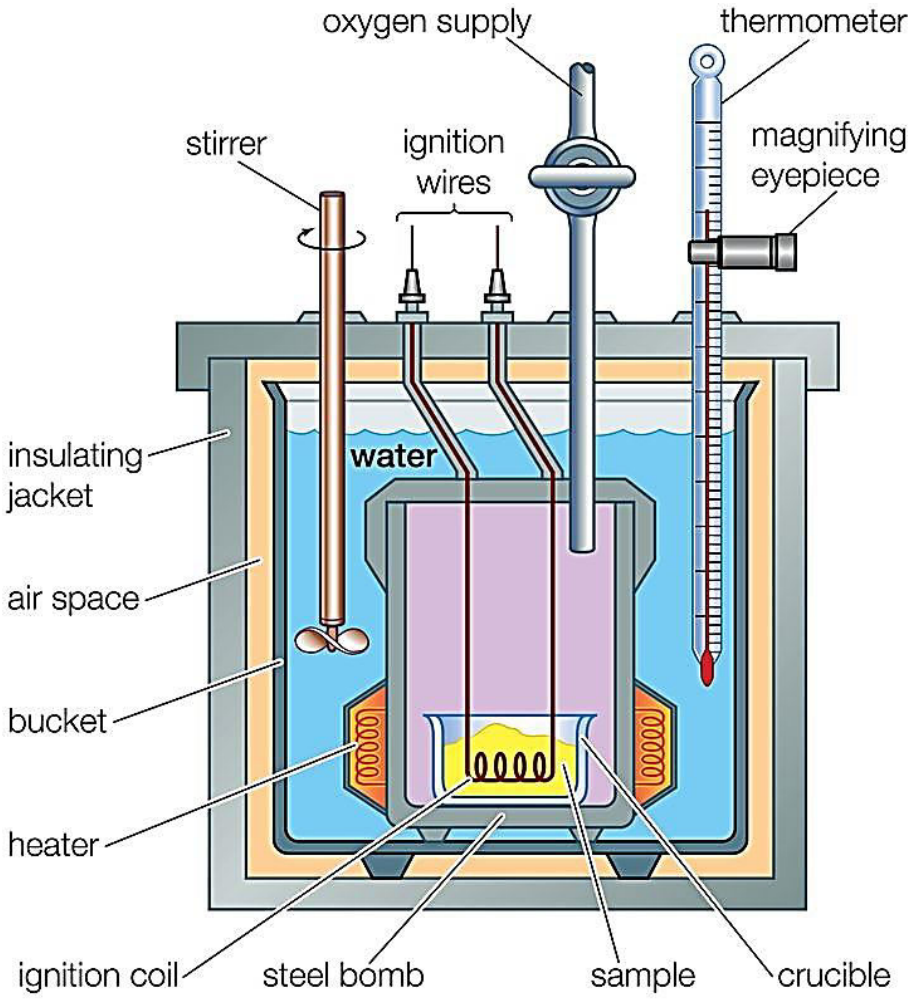
If H is the percentage of hydrogen in fuel,

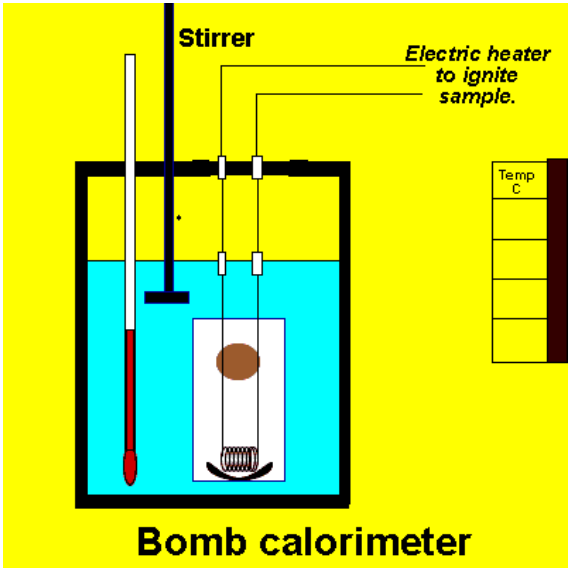
the mass of water produced from 1 g of fuel = (9/100)×H

= 0.09 H

Determination of Calorific Value

Bomb calorimeter





Calculation for HCV

$$HCV = \frac{(W+w)(t_2-t_1) \times \text{Specific heat of water}}{m} \ cal/g$$

m	=	mass of fuel pellet (g)
W	=	mass of water in the calorimeter (g)
w	=	water equivalent of calorimeter (g)
t_1	=	initial temperature of calorimeter
t_2	=	final temperature of calorimeter
HCV	=	Higher/gross calorific value of fuel

Specific heat of water = 1 cal/g °C

$$HCV = \frac{(W+w)(t_2-t_1)}{m} \ cal/g$$

Numerical

0.72 g of a fuel containing 80% carbon, when burnt in a bomb calorimeter, increased the temperature of water from 27.3 °C to 29.1 °C. If the calorimeter contains 250 g of water and its water equivalents is 150 g, calculate the HCV of the fuel. Give your answer in kJ/kg.

Solution:

Here, m = 0.72 g; W = 250 g; w = 150 g; t_1 = 27.3 °C and t_2 = 29.1 °C.

HCV of fuel (L) = $\frac{(W+w)(t_2-t_1)}{m}$ cal/g

1 cal/g = 4.2 kJ/kg

$= \frac{(250+150)(29.1-27.3)}{0.72} = 1000\ cal/g$

= 1000 x 4.2 = **4,200 kJ/kg**

Calculation for LCV

Water Equivalent of the calorimeter

- It is determined by burning a fuel of known calorific value Benzoic acid (HCV = 6,325 kcal/kg) and naphthalene (HCV = 9,688 kcal/kg)

If H is the percentage of hydrogen in fuel,
the mass of water produced from 1 g of fuel = (9/100)×H
= 0.09 H

Heat taken by water in forming steam = 0.09 H× 587 cal

(latent heat of steam = 587 cal/kg)

LCV = HCV – Latent heat of water formed

LCV = [HCV – (0.09 H x 587)] kcal/kg

Numerical - Problem

On burning 0.83 g of a solid fuel in a bomb calorimeter, the temperature of 3,500 g of water increased from 26.5 °C to 29.2 °C. Water equivalent of calorimeter and latent heat of steam are 385.0 g of and 587.0 cal/g, respectively. If the fuel contains 0.7% hydrogen, calculate its gross and net calorific value.

Weight of fuel	=	m	=	?	0.83 g
Weight of water	=	W	=	?	3,500 g
Water equivalent of calorimeter	=	w	=	?	385 g
Final temperature	=	t_2	=	?	29.2 °C
Initial temperature	=	t_1	=	?	26.5 °C
Percentage of hydrogen	=	H	=	?	0.7%
Latent heat of steam	=		=	?	587 cal/g

Numerical

$$\text{HCV of fuel (L)} = \frac{(W+w)(t_2-t_1)}{m} \text{ cal/g}$$

$$= \frac{(3500+385)(29.2-26.5)}{0.83}$$

$$= 12,638 \text{ cal/g}$$

NCV = [GCV – 0.09 H × 587]

= (12,63 8 – 0.09 × 0.7 × 587) cal/g

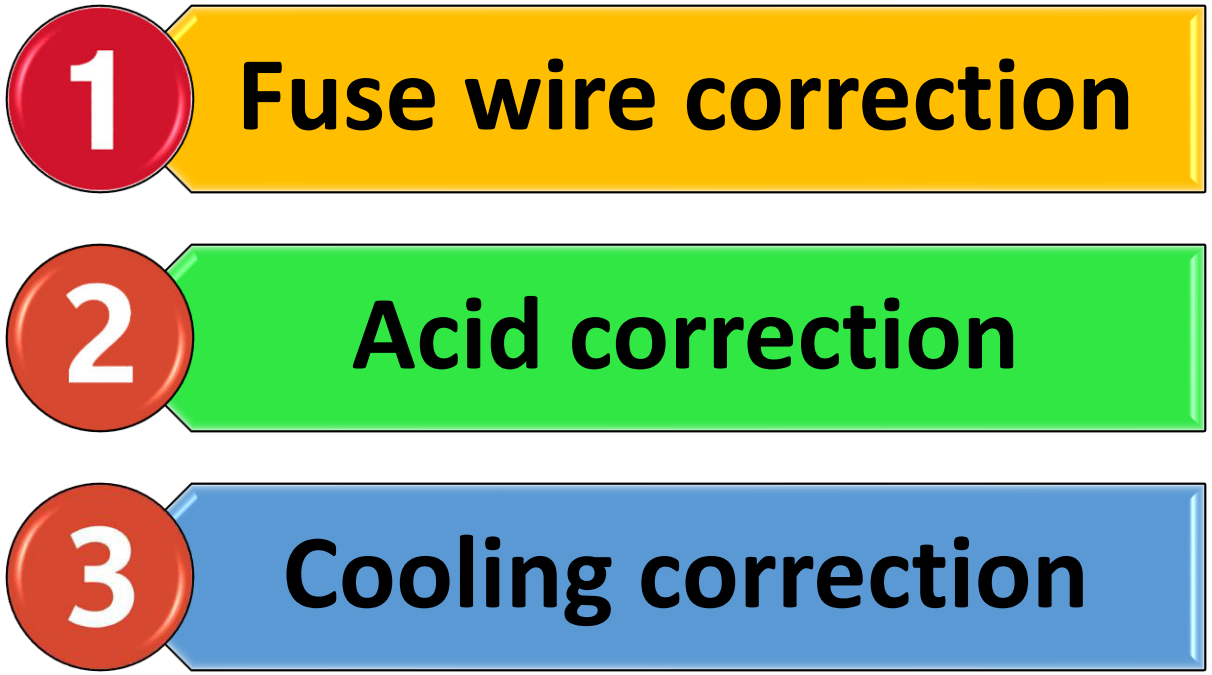
= (12,638 – 37) cal/g

= 12,601 cal/g

Corrections

Corrections

- For accurate results the following corrections are also incorporated



1. Fuse wire correction

Fuse wire correction:

Heat liberated during sparking should be subtracted from calorific value

Fuse wire correction:

1) **As Mg wire is used for ignition, the heat generated by burning of Mg wire is also included in the gross calorific value.**

2) **Hence, this amount of heat has to be subtracted from the total value.**

2. Acid correction

Acid correction:

Fuels containing Sulphur and Nitrogen if oxidized, the heats of formation of H_2SO_4 and HNO_3 should be subtracted (as the acid formations are exothermic reactions)

Acid correction:

During combustion, sulphur and nitrogen present in the fuel are oxidized to their corresponding acids under high pressure and temperature condition.

$$S + O_2 \rightarrow SO_2$$

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad \Delta H = -144{,}000 \text{ cal}$$

$$2N_2 + 5O_2 + 2H_2O \rightarrow 4HNO_3 \qquad \Delta H = -57{,}160{,}000 \text{ cal}$$

2. Acid correction (Cont.)

- The corrections must be made for the heat liberated in the 'bomb calorimeter' by the formation of H_2SO_4 and HNO_3.
- The amount of H_2SO_4 and HNO_3 is analyzed by washings of the calorimeter.
  - For each mL of 0.1 N H_2SO_4 formed, 3.6 calories should be subtracted.
  - For each mL of 0.01N HNO_3 formed, 1.43 calories should be subtracted.

3. Cooling correction:

Cooling correction:

The rate of cooling of the calorimeter from maximum temperature to room temperature is noted. From this rate of cooling [*i.e.* dt (°C/min)] and the actual time taken for cooling (X min) then correction (dt × X) is called cooling correction and is added to the (t_2 - t_1) term.

If the time taken for the water in the calorimeter to cool down from the maximum temperature attained to the room temperature	**= "X" minutes**
Rate of cooling	**= dt (°C/min)**
Cooling correction	**= X × dt**

This should be added to the observed rise in temperature

Calculation after correction

- **HCV - Before corrections**

$$HCV = \frac{(W+w)(t_2-t_1)}{m} \text{ cal/g}$$

- **HCV – After corrections**

$$HCV = \frac{(W+w)[(t_2-t_1) + \text{Cooling correction}] - (\text{Acid correction} + \text{Fuse correction})}{m} \text{ cal/g}$$

Numerical - Problem

A sample of coal contains C = 93%; H = 6% and ash = 1%. The following data were obtained when the above coal was tested in bomb calorimeter.

Weight of coal burnt	**=**	**0.92 g**
Weight of water taken	**=**	**550 g**
Water equivalent of calorimeter	**=**	**2,200 g**
Rise in temperature	**=**	**2.42 °C**
Fuse wire correction	**=**	**10.0 cal**
Acid correction	**=**	**50.0 cal**

Calculate gross and net calorific value of the coal, assuming the latent heat of condensation of steam as 580 cal/g.

Numerical - Solution

Weight of coal burnt	=	**m**	=	**0.92 g**
Weight of water taken	=	**W**	=	**550 g**
Water equivalent of calorimeter	=	**w**	=	**2,200 g**
Rise in temperature	=	**(t_2-t_1)**	=	**2.42 °C**
Fuse wire correction	=		=	**10.0 cal**
Acid correction	=		=	**50.0 cal**
Latent heat of steam	=		=	**580 cal**
Percentage of hydrogen	=	**H**	=	**6%**

Numerical – Solution (Cont.)

(a)

$$GCV = \frac{(W+w)(t_2 - t1) - (\text{Acid correction} + \text{Fuse correction})}{m} \text{ cal/g}$$

$$= \frac{(550+2{,}200) \times (2.42) - (50+10)}{0.92} \text{ cal/g}$$

$$= 7{,}168.5 \text{ cal/g}$$

(b)

$$NCV = [GCV - 0.09 \times H \times \text{latent heat steam}]$$

$$= (7168.5 - 0.09 \times 6 \times 580) \text{ cal/g}$$

$$= 6855.3 \text{ cal/g}$$

Boy's Calorimeter - Principle

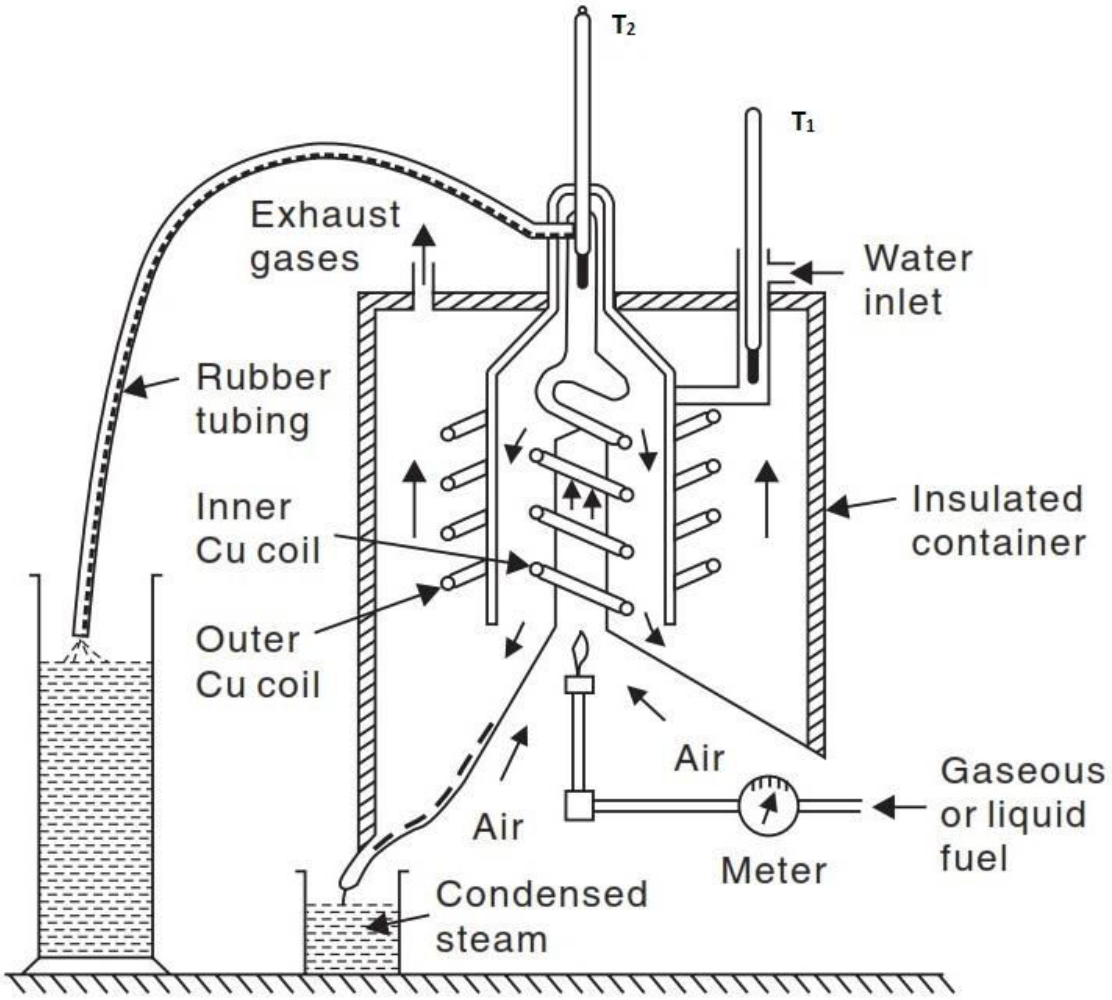
It is used for measuring the calorific value of gaseous (or) liquid fuels.

Principle

- A known volume of gaseous fuel sample is burnt in the combustion chamber of a Boy's calorimeter.
- The released heat is quantitatively absorbed by cooling water, circulated through copper coils surrounding the combustion chamber.
- The mass of cooling water and its rise in temperature are noted.
- The mass of water produced by condensation of steam is calculated.
- The calorific value of the fuel sample is then calculated from these data.

Boy's Calorimeter

32.Boy's Calorimeter_Module_6_(II)



Boy's gas calorimeter

Boy's Calorimeter - Construction

Construction

Boy's calorimeter consists of a combustion chamber surrounded by water tube with two thermometers T_1 and T_2 attached. There is a burner in the chamber, which is connected to a gas tube.

Working

- A known volume of water is passed through the tubes.
- The initial temperature is noted when the two thermometers show the same constant temperature.
- A known volume of the gas (measured using a meter) is passed through the tube and burnt in the combustion chamber.
- The heat liberated is absorbed by the water in the tubes.
- The final temperature of water is noted.
- The gaseous products are cooled and condensed into a measuring jar.

Boy's Calorimeter - Calculation

$$\text{HCV (or) GCV} = W \times S \times \frac{(T_2 \ \ T1)}{V}$$

$$\text{LCV (or) NCV} = \left(\text{GCV} - \frac{m \times 587}{V} \right)$$

V = Volume of the gas burns at STP in certain time (t)

W = Mass of the cooling water used in time (t)

T_1 = Temperature of inlet water

T_2 = Temperature of outgoing water

m = Amount of water collected from condensation in time (t)

S = Specific heat of water

Specific heat of water = 1 cal/g °C

Determination of calorific value

Determination of calorific value

- **Experimental methods**
  1. Bomb calorimeter
  2. Boy's calorimeter

- **Theoretical method**
  - Dulong's formula
    (or)
  - I.A. Davies formula

- The calorific value of fuels (e.g. Coal) is determined theoretically by Dulong's formula or I.A. Davies formula

Dulong's Formula

- The approximate calorific value of a fuel can be determined by knowing the amount of constituents present:
- Gross or higher calorific value (HCV) from elemental constituents of a fuel.

  H = 34500 kcal/kg; C = 8080 kcal/kg; S = 2240 kcal/kg

- Oxygen present in the fuel is assumed to be present as water (fixed hydrogen).

  Available Hydrogen = Total hydrogen - Fixed hydrogen

  = Total hydrogen - 1/8 mass of oxygen in fuel

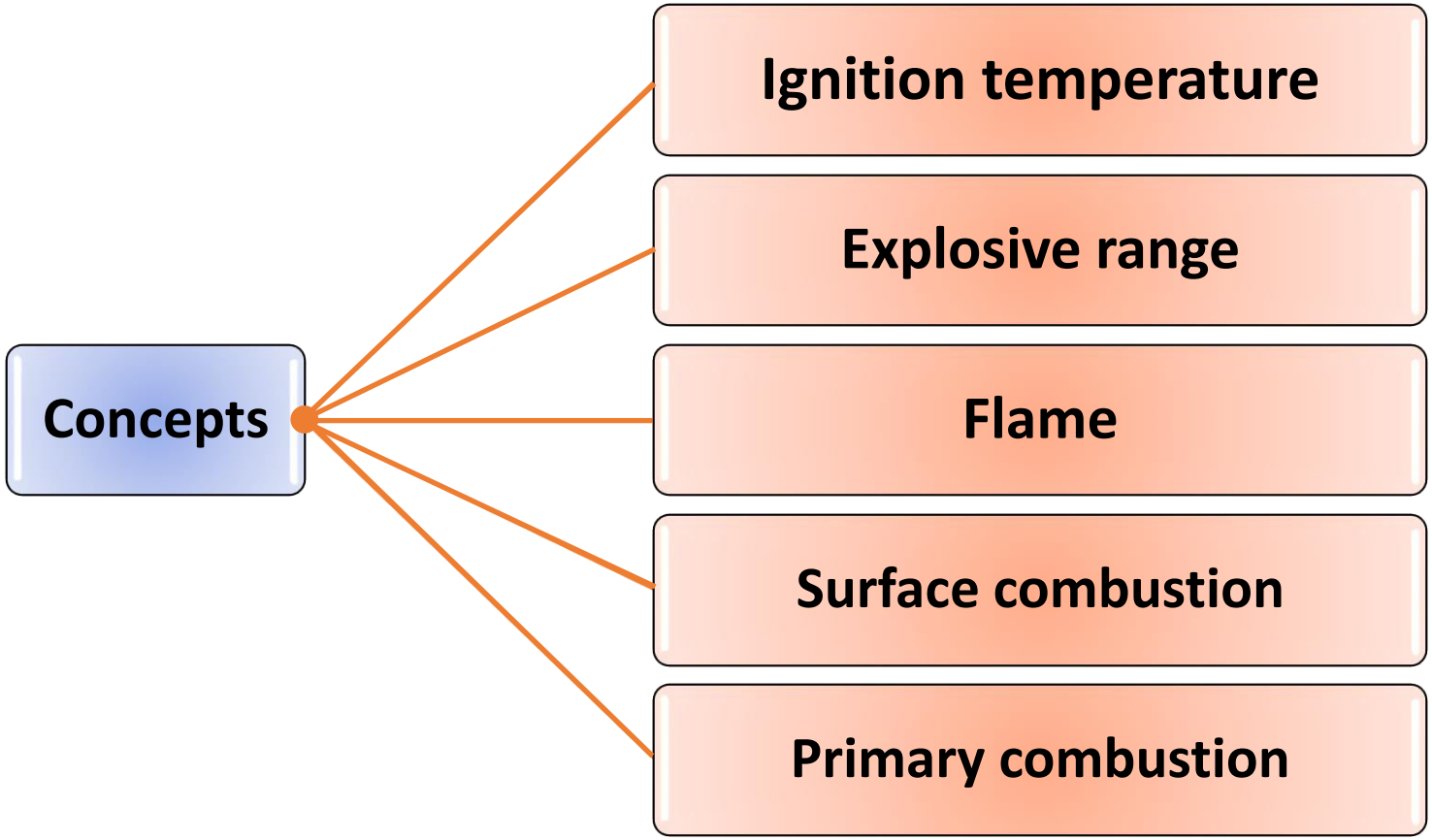
- Dulong's formula for calorific value from the chemical composition of fuel is,

$$HCV = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right] \text{ kcal/kg}$$

Combustion of Fuel

Combustion

- **Combustion** is a process in which oxygen from the air reacts with the elements or compounds to give heat.



Combustion

- As the elements or compounds combine in definite proportions with oxygen, we need to calculate what is ***minimum oxygen or air required*** for the complete combustion of compounds.
- The commonly involved combustion reactions are;

i) $C + O_2 \rightarrow CO_2$

ii) $2H_2 + O_2 \rightarrow 2H_2O$

iii) $S + O_2 \rightarrow SO_2$

iv) $2CO + O_2 \rightarrow 2CO_2$

v) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

vi) $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

vii) $2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$

Combustion - Calculation of air quantities

✓ Substances always combine in definite proportions.

C (s)	+	O_2 (g)	→	CO_2 (g)
12		32		44

✓ Air contains 21% of oxygen by volume & 23% of oxygen by mass.

1 *kg* of oxygen is supplied by $\frac{1 \times 100}{23}$ = 4.35 kg of air

1 m^3 of oxygen is supplied by $\frac{1 \times 100}{21}$ = 4.76 m^3 of air

✓ 28.94 g/mol is taken as the molecular mass of air

- Since air has 23% by weight or 21% by volume of oxygen

- Minimum weight of air needed for complete combustion = Net O_2 x 100/23 g
- Minimum volume of air needed for complete combustion = Net O_2 x 100/21 g

Combustion calculation procedure

Combustion equation	Wt. of Oxygen needed	Vol. Of Oxygen needed
$C + O_2 \rightarrow CO_2$ "x" g or m^3	$x \times 1 \times \frac{32}{12}$	$x \times 1$
$H_2 + 0.5\ O_2 \rightarrow H_2O$ "y" g or m^3	$y \times 0.5 \times \frac{32}{2}$	$y \times 0.5$
$CO + 0.5\ O_2 \rightarrow CO_2$ "z" g or m^3	$z \times 0.5 \times \frac{32}{28}$	$z \times 0.5$
$S + O_2 \rightarrow SO_2$ "p" g or m^3	$p \times 1 \times \frac{32}{32}$	$p \times 1$
$CH_4 + 2\ O_2 \rightarrow CO_2 + 2H_2O$ "q" g or m^3	$q \times 2 \times \frac{32}{16}$	$q \times 2$
$C_2H_6 + 3.5\ O_2 \rightarrow 2CO_2 + 3H_2O$ "r" g or m^3	$r \times 3.5 \times \frac{32}{30}$	$r \times 3.5$

Combustion- Numerical problem

Question: How much air is required to burn 1 kg of pure carbon?

Solution: M. Wt. of O_2 = 32

This reacts with C, M. Wt. = 12

C (s)	+	O_2 (g)	→	CO_2 (g)
12		32		44
x = 1000 g		m_{Oxygen} = ?		

Wt. of Oxygen needed = $m_{Oxygen} = x \times 1 \times \frac{32}{12}$

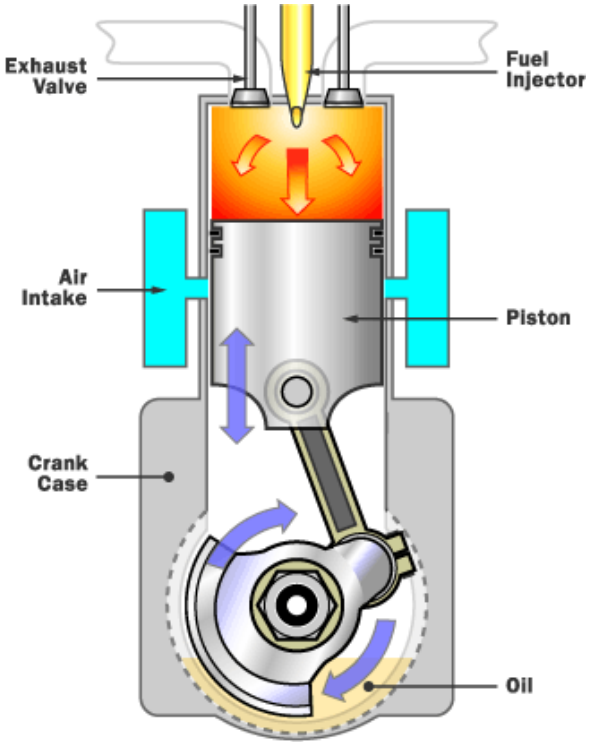
$$m_{Oxygen} = 1000 \times 1 \times \frac{32}{12}$$

= 2667 g (or) 2.667 kg of O_2

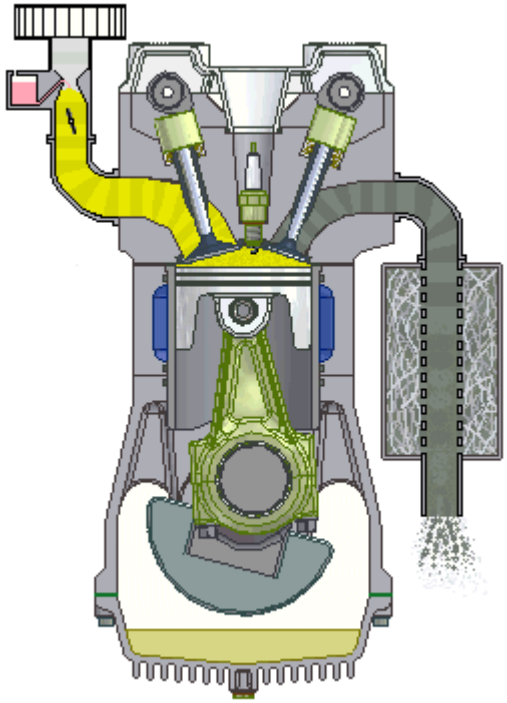
But, air contains only 23% of O_2 by weight

Mass of air required to burn 1 kg of pure carbon = $\frac{100 \times 2.667}{23}$ = 11.59 kg

Knocking



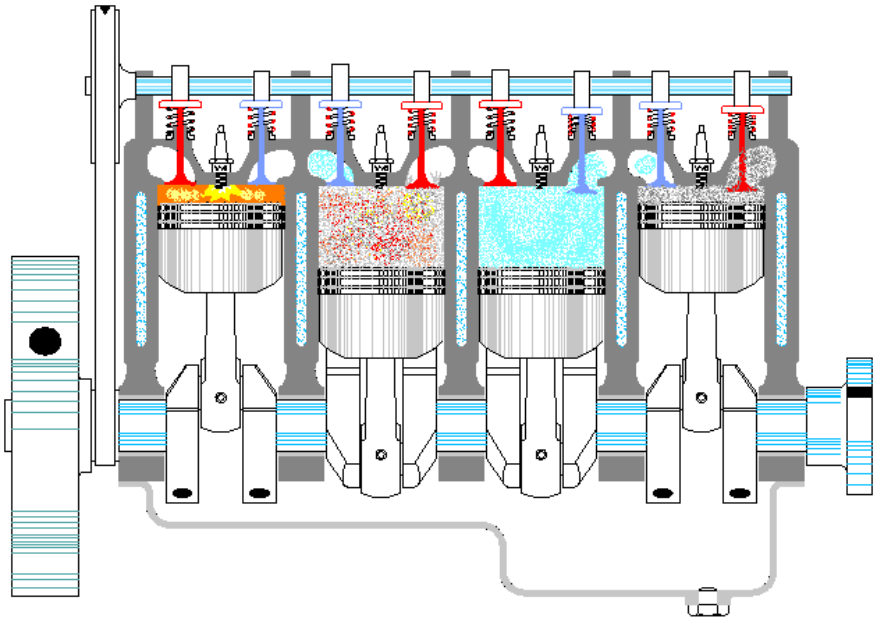
IC engine



An **internal combustion engine** (ICE) is a heat **engine** in which the **combustion** of a fuel occurs with an oxidizer (usually air) in a **combustion** chamber that is an integral part of the working fluid flow circuit

IC engine

- In an internal combustion engine, a mixture of gasoline vapour and air is used as a fuel.
- After the initiation of the combustion reaction by spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture, thereby the expanding gas drives the piston down the cylinder.



IC engine – Compression ratio

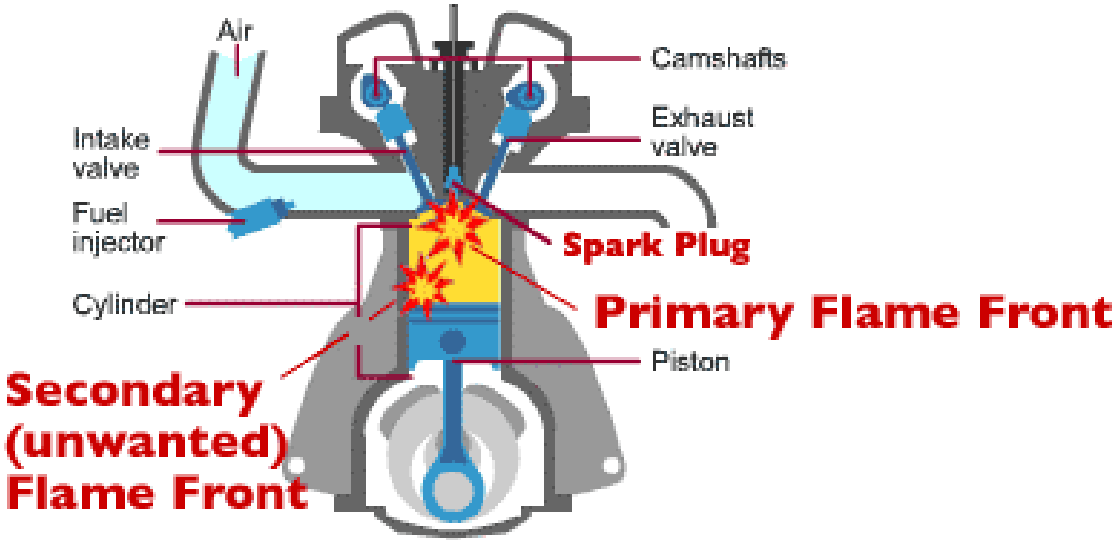
- **The ratio of the gaseous volume in the cylinder (V_1) at the end of the suction stroke to the volume (V_2) at the end of compression-stroke of the piston is known as the 'compression ratio'.**

V_1 being greater than V_2, the CR is > 1

- The CR indicates the extent of compression of the fuel-air-mixture by the piston.
- Efficiency of IC engine increases with compression ratio.

IC engine – Knocking

- In certain circumstances, due to the presence of some constituents in the gasoline used, the rate of oxidation becomes so great that the last portion of the fuel-air mixture gets ignited instantaneously producing an explosive violence, known as '**knocking**'.



Knocking – Rattling noise or sharp metallic noise produced by internal combustion engine
– Loss of energy and engine lifetime

Knocking in IC engine

33.IC Engine - Knocking_Module_6_(ii)

Knocking – Reasons and Effects

Reasons

- If the IC Engine chamber is not getting the appropriate mixture of air and fuel combining together for combustion, then it will result in inconsistent fuel burn.

Chemical structure and Knocking

- The tendency of fuel constituents to knock is in the following order;

Straight chain paraffins > **Branched chain paraffins (iso-paraffin)** > **Olefins** > **Cyclo paraffins (naphthenes)** > **Aromatics**

Effects

- **The knocking results in loss of efficiency, since this ultimately decreases the compression ratio.**
- **The cylinder wall and piston get damaged.**

Knocking – Gasoline & Diesel fuel

Octane Number Vs Cetane Number

Octane number is a measure of the performance of a fuel	Cetane number is the measure of the delay of the ignition of a fuel
Important for predicting the knocking of an engine	Important for predicting the ignition of an engine
Given for gasoline	Given for diesel
Octane rating is done considering the octane number of isooctane as 100	Cetane rating is done considering the ignition of cetane

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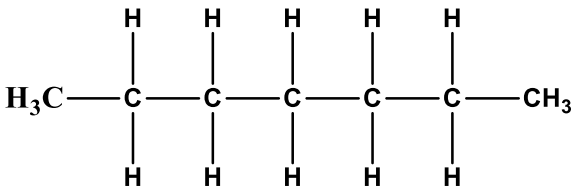
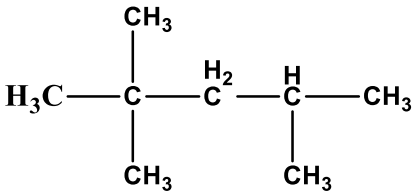
Octane Number

- The most common way of expressing the **knocking characteristics of a combustion engine fuel is by 'octane number'**, introduced by Edger.
- A measure of the resistance of petrol and other fuels to autoignition n-heptane, knocks very badly and hence, its anti-knock value has arbitrarily been given zero.
- Isooctane (2, 2, 4-trimethyl pentane) gives very little knocking , so its anti-knock value has been fixed as 100.
- Octane number is defined as the % of isooctane in a mixture of n-heptane and isooctane which has the same knocking characteristics of the petrol under the same set of conditions.



n-Heptane

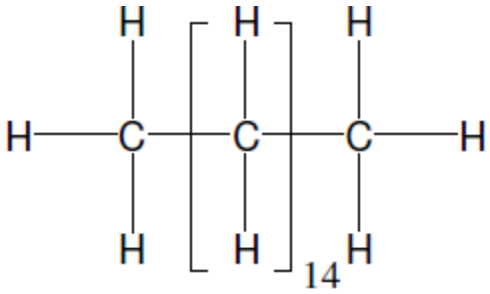


Isooctane

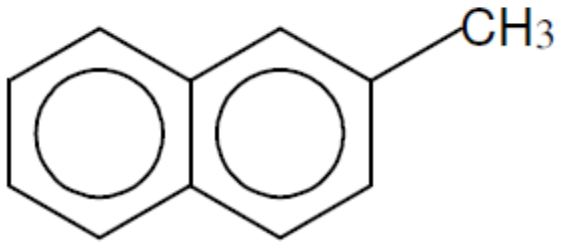
Greater the octane number, greater is the resistance of knocking

Cetane Number

- **The suitability of a diesel fuel is determined by its cetane value**, which is the percentage of hexadecane in a mixture of hexadecane and 2-methyl naphthalene, which has the same ignition characteristics as the diesel fuel sample, under the same set of conditions.



n-hexadecane (cetane No.=100)



2-Methyl naphthalene (cetane No.=0)

The cetane number of a diesel fuel can be raised by the addition of small quantity of certain "pre-ignition dopes" like alkyl nitrites such as ethyl nitrite, iso-amyl nitrite, acetone peroxide.

Anti-knocking Agents

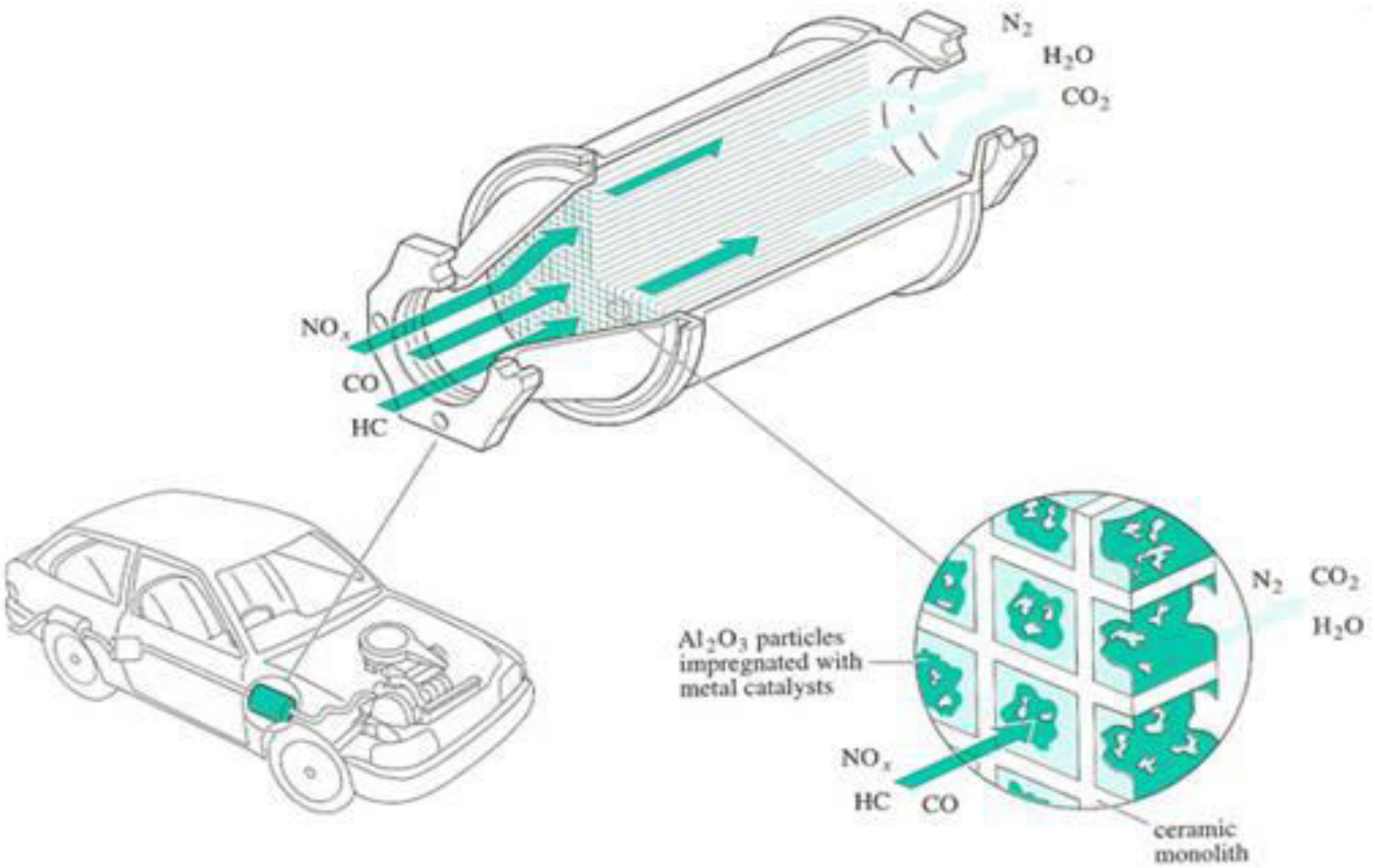
Improvement of anti-knock characteristics of a fuel

- The octane number of poor fuels can be raised by the addition of tetra ethyl lead $(C_2H_5)_4Pb$ or TEL and diethyl telluride $(C_2H_5)_2Te$.
- TEL is converted into a cloud of finely divided lead and **lead oxide** (litharge) particles in the cylinder, thereby reducing the oxidation.
- Deposit of lead oxide is harmful to the engine life, **ethylene dibromide** is added to remove the lead oxide formed as lead bromide along with exhaust gases.
- **Emission of Lead:** **Damages the environment**

Unleaded petrol: Alternative methods

- Addition of high octane compounds like isopentane, isooctane, ethyl benzene, isopropyl benzene, **methyl tertiary butyl ether** (MTBE). Among these MTBE is more preferred because it contains oxygen in the form of ether group and supplies oxygen for the combustion of petrol in internal combustion engines there by reducing the extent of peroxy compound formation.

Three-way catalytic converter



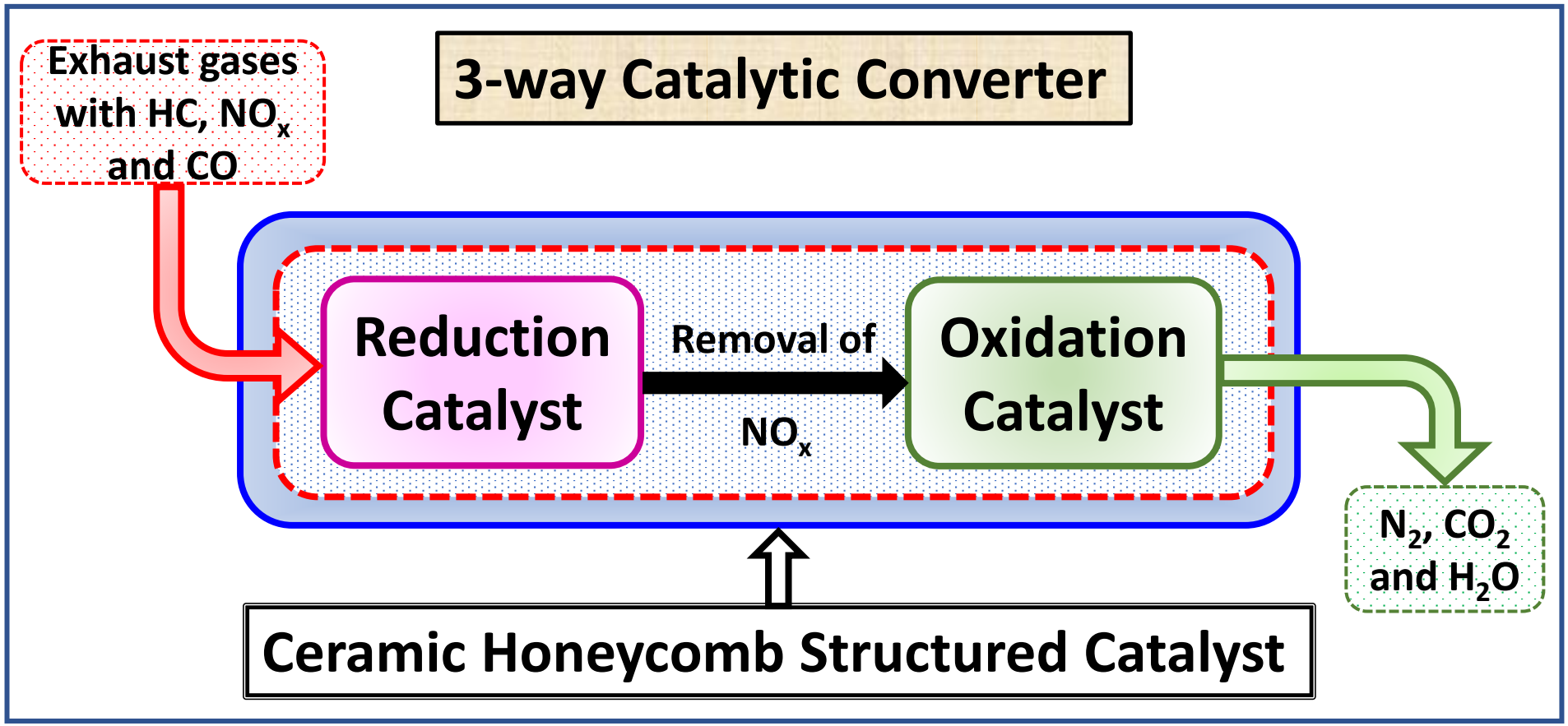
Three-way catalytic converter

Components

- The current three-way catalyst is generally a multicomponent material, containing the precious metals rhodium, platinum and (to a lesser extent) palladium, ceria (CeO_2), γ-alumina (Al_2O_3), and other metal oxides.
- It typically consists of a ceramic monolith of cordierite ($2Mg{\cdot}2Al_2O_3{\cdot}5SiO_2$) with strong porous walls enclosing an array of parallel channels.
- For example, Cordierite is used because it can withstand the high temperatures in the exhaust, and the high rate of thermal expansion encountered when the engine first starts – typically, the exhaust gas temperature can reach several hundred degrees in less than a minute.
- The reduction catalyst is made of platinum and rhodium while the oxidation catalyst is made of platinum and palladium. Both the catalysts have a ceramic honeycomb structure.

Working of Three-way catalytic converter

- A three-way catalytic converter makes use of two catalysts to convert harmful gases to harmless gases.
- They are: **Reduction Catalyst** & **Oxidation Catalyst**



Function of Three-way catalytic converter

Stage 1 – Reduction Catalyst:

- The exhaust gases are first sent over the reduction catalyst (which is made of platinum and rhodium). It converts oxides of nitrogen (NO_x) to nitrogen (N_2) and oxygen (O_2).

$$2NO \rightarrow N_2 + O_2$$

$$2NO_2 \rightarrow N_2 + O_2$$

Stage 2 – Oxidation Catalyst:

- Exhaust gases that are free of oxides of nitrogen (NO_x) are then sent over the oxidation catalyst (made of platinum and palladium). The oxidation catalyst coverts carbon-monoxide (CO) and hydrocarbons (HC) in the gases into carbon-di-oxide (CO_2) and water (H_2O).

$$2CO + O_2 \rightarrow 2CO_2$$

$$HC + O_2 \rightarrow CO_2 + H_2O$$