Module- 4 Energy Science

(Fuels & Combustion; Batteries)

Contents:*Types of fuels, Calorific value, Determination of Calorificvalue, Combustion and its calculations, Solid fuel: Coal analysis (Proximateand ultimate analysis), Liquid fuels: IC engine fuel, concept of knocking, antiknocking, octane No and cetane No, Fractional Distillation of petroleum, Cracking of heavy oils; Elementary ideas on some gaseous fuels (Naturalgas, Water gas, Producer gas, LPG) (Synthesis is excluded), Batterytechnology – Fundamentals of primary & Secondary cells, Rechargeablebatteries: Lead acid storage battery, Lithium ion battery, Fuel cells: principles, applications. Elementary idea on Photo-voltaics.*

Course Outcome: Classify various fuels based on combustion parameters and understand the working principleof various batteries.

1.0 Introduction

In recent years our dependency on energy has enhanced a lot as a result of the increase in the standard of living and rapid technological advancement. The various types of fuels like liquid, solid and gaseous fuels are available for firing in boilers, furnaces and other combustion equipments. The selection of right type of fuel depends on various factors such as availability, storage, handling, pollution and landed cost of fuel. The knowledge of the fuel properties helps in selecting the right fuel for the right purpose and efficient use of the fuel.

Process industries, businesses, homes, and transportation systems have vast heat requirements that are also satisfied by *combustion* reactions. The energy usually comes from the fuels like petroleum, coal and natural gas known as *Fossil* *fuel*. Since these sources of energy will never last forever hence their proper utilization is the main concern these days.

** ***Combustion***is the conversion of a substance called a *fuel* into chemical compoundsknown as *products of combustion* by combination with an *oxidizer*. The combustionprocess is an *exothermic* chemical reaction, i.e., a reaction that releases energy as itoccurs.

** ***Fossil fuel:***They are formed by the decay of vegetable and animal matter over many thousands of years under conditions of high pressure and temperature and with a deficiency or absence of oxygen.

2.0 Fuel and its classification

A fuel can be defined as *any combustible substance which during combustion gives large amount of industrially and/or domestically useful heat*. The heat evolved by burning of fuels is used for heating purposes, in locomotive engines, in internal combustion engine, etc. We use coal as a reducing agent in metallurgical industry. Examples of some fuels are coal, coke, LPG, CNG, petrol, diesel, etc.

Classification of fuels:

1. **Based on their occurrence:** Fuels are classified as A. *natural or primary* and B. *artificial or secondary* fuels.
   A. Natural fuels: They are found in nature as such. Examples are coal, wood, petroleum and natural gas.
   B. Artificial fuels: They are prepared from primary fuels. Examples are coke, petrol, diesel, coal gas, etc.

2. **Based on their physical state of aggregation:** Fuels are classified as solid, liquid and gaseous.
   Solid fuels: Coal, coke, wood
   Liquid fuels: Petroleum, petrol diesel, kerosene
   Gaseous fuel: CNG, LPG, coal gas, biogas

3.0Calorific Value (CV) or Heat value

The CV is the total quantity of heat liberated from combustion of a unit mass or unit volume of the fuel in air or oxygen. So, it is the measurement of produced heat or energy. It is measured either as Gross Calorific Value (GCV) or Net Calorific Value (NCV). The difference being the latent heat of condensation of the water vapour produced during the combustion process.

Units of calorific value:

For solid fuels: cal/g; Kcal/Kg

For liquid or gaseous fuels: Kcal/m^3

Gross calorific value (GCV): Gross calorific value (GCV) assumes all vapour ($H_2O_{(g)}$) produced during the combustion process is fully condensed. So, *it is total amount of heat liberated when unit mass or unit volume of the fuel has been burnt completely and products of combustion (CO_2& H_2O) are cooled to RT.*It is also called as Higher Calorific Value (HCV).

Net calorific value (NCV): Net calorific value assumes the water leaves with the combustion products without fully being condensed. So, So, *it is total amount of* *heat liberated when unit mass or unit volume of the fuel has been burnt completely and products of combustion (CO_2& H_2O) are allowed to escape.* It is also called as Lower Calorific Value (LCV).

Fuels should be compared based on the NCV.

Relationship between GCV and NCV:

NCV = HCV- Latent heat of water vapour formed

= HCV – 0.09H x 587; where H = % H in the fuel.

So, for a fuel without H-content, NCV = HCV

Calorific value can be determined using a **Bomb Calorimeter.**

4.0 Theoretical calculation of Calorific value by Dulong's Formula:

Assumption: Calorific value of a fuel is the sum of the calorific values due to all the components (C,H, S) present in the fuel. It is also assumed that if oxygen is present in the fuel then it is present in the combined form with hydrogen as H_2O.

The GCV of the component C, H, and S are 8080,34500, and 2240 cal/g, respectively.

GCV = 1/100[8080C + 34500(H-O/8) + 2240S] in Kcal/Kg

Where, C = % Carbon in the fuel; H = % Hydrogen in the fuel, and %S= % Sulphur in the fuel

Solved Examples:

Example-1 Calculate the GCV and NCV of a coal sample having the following composition: C = 80%, H=7%, O=3%, S=3.5%, N=2.1% and ash=4.4% as per proximate analysis.

Solution: N and ash are non-combustible matter, not take part in calculation process

GCV = 1/100[8080C + 34500(H-O/8) + 2240S]

= 1/100[8080x80 + 34500(7-3/8) + 2240 x 3.5] = 8828 cal/g

NCV = HCV – 0.09H x 587 = 8828-0.09x7x587 = 8458 cal/g.

Example-2 Calculate the HCV and LCV of a coal sample having the following composition: C = 75%, H=5.2%, O=12.1%, N=3.2% and ash=4.5%

Solution: N and ash are non-combustible matter

GCV = 1/100[8080C + 34500(H-O/8) + 2240S]

= 1/100[8080x75 + 34500(5.2-12.1/8) + 2240 x 0] = 7332.2 cal/g

NCV = HCV – 0.09H x 587 = 8828-0.09x5.2x587 = 7057.5 cal/g.

5.0 Characteristics of a good fuel

A good fuel should have the following characteristics:

1. It should have High Calorific Value.
2. It should have moderate ignition temperature.

3. It should have low moisture content.
4. It should have low non-combustible matter content.
5. It should have moderate rate of combustion.
6. It should have low cost.
7. It should be easy to transport.
8. It should not emit harmful products.
9. It should have low volatile matter content.

Q. 1. Define calorific value.

Ans. The CV is the total quantity of heat liberated from combustion of a unit mass or unit volume of the fuel in air or oxygen.

Q. 2. 5 Kg of a solid fuel generates 55,000 Kcal of heat. Find its calorific value (CV).

Ans: CV = 55,000/5 = 11,000 Kcal/Kg

Q.3 When 100 m^3 gaseous fuels like LPG undergoes combustion, it generates 110,000 Kcal of heat. Find its CV.

Ans. CV = 110,000/100 = 1100 Kcal/m^3

Q.4 Mention the condition for which HCV will be same as LCV?

Ans. When % H = 0 in a fuel then HCV = LCV

Q. 5. Mention some characteristics of good fuel. (Medium type, 3 marks)

Ans. Refer section 5.0

Q.6.A good fuel should contain very less amount of moisture. Give reason.

Ans. During burning, moisture takes some of the liberated heat in the form of latent heat of vapourization. Therefore, it lowers the effective CV of fuel.

Q. 7 . Distinguish between GCV and NCV.

Ans. Refer section 3.0

Q8. What is meant by Ignition temperature?

Ans. It is the lowest temperature to which the fuel is pre-heated so that it starts burning smoothly.Or it is the minimum temperature at which the combustion is self-supporting.

Q. 9. Why should an ideal fuel have moderate ignition temperature?

Ans. Low ignition temperature can cause fire hazards and involves danger in fuel storage and transport; while high ignition temperature causes difficulty in starting ignition of fuel. Hence, an ideal fuel should have moderate ignition temperature.

Q. 10 What are secondary fuels?

Ans. Fuels which are prepared by artificially from primary fuels are called secondary or artificial fuels. Examples are coke, charcoal, petrol, etc.

Q. 11 Why is NCV less than GCV?

Ans. As the combustion products are not condensed in NCV calculation so lesser amount of heat is available. It is less than GCV by the amount of latent heat of steam formed during the complete combustion of one unit of the fuel.

NCV = HCV- Latent heat of water vapour formed

$= \text{HCV} - 0.09\text{H} \times 587$; where H = % H in the fuel.

Combustion Calculation

✓ *Important points*

1. Substances always combine in definite proportions and these proportions are determined by the mol. masses of the substances involved and the products formed.

$$C + O_2 \rightarrow CO_2$$

   Here, 12 g of C combines with 32g of oxygen to form 44g of carbon dioxide

   (Mass proportion ratio 12:32:44)

   For gaseous fuel hydrogen, $H_{2(g)}$ + $1/2O_{2(g)} \rightarrow H_2O(g)$, 1 vol. of hydrogen combines with ½ vol. of oxygen to form 1 vol of water.

2. 22.4 L of any gas at STP (0 ^{0}C and 1 atm.) has a mass equal to its 1 mol. Thus, 22.4 L of O_2 gas at STP will have a mass of 32g. 22.4 L of Air at STP will have a mass of 28.94 g.

3. Mol. Mass of air is taken as 28.94 g/mol.
4. Air contains 21% of oxygen by volume and 23% by mass. This means 100 g of air contain 23 g of oxygen and 100 L of air contains 21 L of oxygen.

Most Commonly involved combustion Reactions:

1. **$H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O(g)$**
2. **$C + O_2 \rightarrow CO_2$**
3. **$S + O_2 \rightarrow SO_2$**
4. **$CO + 1/2O_2 \rightarrow CO$**
5. **$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$**
6. **$C_2H_{6(g)} + 7/2O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$**

7. **$C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(g)}$**
8. **$C_2H_{2(g)} + 5/2O_{2(g)} \rightarrow 2CO_{2(g)} + H_2O_{(g)}$**

Solved Examples:

A. For Solid fuels

Example-1 *Calculate the weight and volume ofair required for the combustion of 5 kg of coke.*

Solution: **Weight of air required:**

C (coke) + $O_2 \rightarrow CO_2$

12g of C required 32g of oxygen

5000 g of C will need = 32/12 x 5000 = 13333.33 g of O_2

Air reqd. = (100/23) x 13333.33 = **57971 g**

Volume of air required:

We know that 28.94 g of air occupies volume 22.4 L

57971 g will occupy = (22.4/28.94) x 57971 g = **44870.43 L**

Example-2*A sample of coal was found to have the following percentage composition: C = 80 %, H =7%, O=5 %, N=3 %, S =2 % and rest is ash. Calculate the minimum air required for complete combustion of 1 kg of coal.*

Solution: Reactions:

1. $C + O_2 \rightarrow CO_2$ (here, 12 g of C needs 32g of O_2)
   12g 32g
2. $H_2 + 1/2O_2 \rightarrow H_2O$ (here 2 g of hydrogen needs 16 g of oxygen)
   2g 16g
3. $S + O_2 \rightarrow SO_2$ (here, 32 g of C needs 32g of O_2)
   32g 32g

As per the data given: 1kg = 1000g of coal contains 800g C, 70g H,50g O, 30g N, 20g S, and 30g ash. (*N and ash are non-combustible matter*)

So, air needed = wt of [C x (32/12) + H x (16/2) + S x (32/32) – O] x 100/23

= [(800 x 32/12) + 70 x (16/2) + 20 x 1 – 50]x 100/23= (2133.33 + 560 + 20 – 50) x 100/23

= 2663.33 x 100/23 =11,579.69 g = **11.57 kg**

Example-3*A coal sample was found to have the following % composition: C = 75%, H=5.2%, O=12.1%, N=3.2% and ash=4.5%.*

(i) ***Calculate the weight of air required for complete combustion of 1 kg of coal.***

(ii) ***Find volume of air needed for it.***

(iii) ***Find HCV and NCV.***

Solution:

As per the data given: 1kg = 1000g of coal contains 750 g C, 52gH,121 g O, 32g N, and 32 g ash. (*N and ash are non-combustible matter*)

As no S in the sample, % S = 0

(i). So, wt of air needed = wt of [C x (32/12) + H x (16/2) + S x (32/32) – O] x 100/23

= [(750 x 32/12) + 52 x (16/2)– 121]x 100/23 = (2000 + 416– 121) x 100/23

= 2295 x 100/23 =**9978 g = 9.978 kg**

(ii) Volume of air:

We know that 28.92 g air occupies 22.4 L

9978 g of air will occupy = (22.4/28.92) x 9978 L = 7728.46 L

(ii) **GCV** = 1/100[8080C + 34500(H-O/8) + 2240S]

= 1/100[8080 x 75 + 34500(5.2-12.1/8) + 2240 x 0] = **7332.2 cal/g**

NCV = HCV – 0.09H x 587 = 8828-0.09x5.2x587 = **7057.5 cal/g.**

Example-4

A coal sample gave the following analysis: C = 66 %, H = 4 %, O = 7 %, N = 2 %, S = 3 %, moisture = 8 % and ash = 10 %. Determine the amount of air needed if 1 Kg of coal is burnt with 25% excess air.

Ans. As per the data given: 1kg = 1000g of coal contains 660 g C, 40g H,70 g O, 20g N, 30 g S, 80 g moisture and 100 g ash. (*N , moisture and ash are non-combustible matter*)

Air needed = = wt of [C x (32/12) + H x (16/2) + S x (32/32) – O] x 100/23 x 125/100

= [(660 x 32/12) + 40 x (16/2) + 30 x (32/32) – 70] x 100/23 x 125/100

= (1760 + 320 + 30 – 70) x 100/23 x 125/100 = 11,086.956 g

B. For gaseous fuels

Example-1 ***Calculate the volume of air needed for the complete combustion of 100 L of hydrogen gas.***

Solution: Combustion rxn: $H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)}$

1 vol½vol

It means, 1 L of hydrogen needs ½ L of oxygen

So, 100 L needs = 50 L O_2

Vol of air needed = vol of Oxygen x (100/21) = 50 x 100/21 = **238.095 L**

Example-2 ***A gaseous fuel has the following composition by volume: CH_4 = 70 %, CO_2 = 20 % and N_2 = 10 %. Find the volume of air required for the complete combustion of 1 m^3 of this fuel.***

Solution: CO_2 and N_2 gas are non-combustible. 1 m^3 of gas contains 0.7 m^3 CH_4

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$

Here, 1 vol.of methane gas needs 2 vol of oxygen

Then, 0.7 m^3 CH_4 needs = 2 x 0.7 = 1.4 m^3 O_2

Vol of air needed for 1 m^3 of gas = 1.4 x 100/21 = **6.66 m^3**

Example-3 ***A gaseous fuel has the following composition by volume: CH_4 = 70 %, H_2 = 20 % CO_2 = 5% and N_2 = 5 %. Find the volume of air required if 1 m^3 of this fuel is burnt with 40% excess air.***

Solution: **:**1 m^3 of gas contains 0.7 m^3 CH_4, 0.2 m^3 H_2, 0.05 m^3 CO_2 *and* 0.05 m^3 N_2.

Here, CO_2 and N_2 gas are non-combustible.

Combustion equation	**Volume of Oxygen needed**
$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$	0.7 x 2 = 1.4 m^3
$H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)}$	0.2 x ½ = 0.1 m^3
	Total Vol. of O_2 = 1.4 + 0.1 = 1.5 m^3

Vol. of air needed = Vol of O_2 x 100/21 x 140/100 = 1.5 x 100/21 x 140/100 = 10 m^3 = 10 x 10^3 L = 10^4 L

Example-4 ***A gaseous fuel has the following composition by volume: CH_4 = 80 %, H_2 = 5%, O_2 = 10 % and N_2 = 5 %. Find the volume and weight of air required if 1 m^3 of this fuel is completely burnt.***

Solution: Solution: 1 m^3 of gas contains 0.8 m^3 CH_4, 0.05 m^3 H_2, *0.1 m^3 O2, and* 0.05 m^3 N_2. *Here,* N_2 gas is non-combustible.

Combustion equation	Volume of Oxygen needed
$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$	0.8 x 2 = 1.6 m^3
$H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)}$	0.05 x ½ = 0.025 m^3
	Total Vol. of O_2 = 1.4 + 0.025 = 1.625 m^3 **Fuel contains O_2 = 0.1 m^3** **So, net O_2 needed = 1.625-0.1 = 1.525 m3**

Vol. of air needed = Vol of O_2 x 100/21 x 140/100 = 1.525 x 100/21 = 7.261 m^3= 7.261 x 10^3 L

Wt. of air needed:

We know that 22.4 L of air weigh 28.92 g

So, 7.261 x 10^3 L will weigh = (28.92/22.4) x 7.261 x 10^3 = 9.374 x 10^3 g = 9.374 Kg.

Solid Fuels

Solid fuel refers to various forms of solid material that can be burnt to release energy, providing heat and light through the process of combustion. Solid fuels have been used throughout human history to create fire and it is still in extensive use all over the world in the present day. They are of two types: 1. Natural (wood, coal) and 2. Artificial (coke, paddy straw, corn, etc.).

Characteristics of a good solid fuel:

1. High calorific value, 2. Low moisture content, 3. Low cost, 4. Low S & P content, 5. Low ash content, 6. Low volatile matter content, etc.

Advantages of solid fuels: 1. They are easy to transport; 2. Easy to store; 3. Low cost; 4. Possess moderate ignition temperature.

Disadvantages of solid fuels: 1. Ash content is high, 2. Thermal efficiency is low, 3. Burn with clinker formation, 4. Calorific value is lower as compared to liquid fuels, 5. Causes lot of air pollution

Coal and its analysis

Coal is a fossil fuel. It is a highly carbonaceous matter that has been formed as result of anaerobic microbial decomposition of cellulosic materials of plants under high temperature and pressure condition. Coal is classified into three major types namely anthracite, bituminous, and lignite. Anthracite is the highest rank coal with calorific value ~8700 cal/g. The common coals used in Indian industry are bituminous.

Selection of coal: For the selection of coal for different uses, the following factors are taken into consideration:

1. Calorific value should be high
2. Moisture content should be low
3. Ash content should be low
4. Calorific intensity should be high.
5. S, As, and P content should be low
6. Should have coking quality
7. Fusion temp. of ash should be high (> 1400 ^{0}C)
8. Should be reactive towards steam

Analysis of coal

There are two methods: (A) ultimate analysis and (B) proximate analysis. **The proximate analysis determines only the fixed carbon, volatile matter, moisture and ash percentages whereas the ultimate analysis determines all coal component elements, solid or gaseous.** The ultimate analysis is determined in a properly equipped laboratory by a skilled chemist.

A. Proximate Analysis: The proximate analysis determines only the fixed carbon, volatile matter, moisture and ash percentages using simple apparatus.

1. **Measurement of Moisture**

Determination of moisture is carried out by placing a sample of powdered raw coal of size 200-micron size in a crucible and it is placed in the oven kept at 108±2°C along with the lid for half an hour. Then the sample is cooled to room temperature and weighed again. The loss in weight represents moisture.

$$\% \text{ Moisture} = (\text{loss in wt/wt of coal}) \times 100$$

2. **Measurement of Volatile Matter (VM)**

After the removal of moisture, dried sample of coal is then covered with a lid is placed in an electric furnace maintained at 900 °C. The crucible is taken out after 10 min of heating. The sample is cooled and weighed. Loss in weight is reported as VM.

$$\% VM = (\text{loss in wt due to removal of VM/wt. of coal}) \times 100$$

3. **Measurement of Ash**

The cover from the crucible used in the last test is removed and the crucible is heated in a furnace maintained at 750 ^{0}C until all the carbon is burned. The residue is weighed, which is the incombustible ash.

$$\% Ash = (\text{wt. of ash/wt. of coal}) \times 100$$

4. **Fixed Carbon (FC)**

In actual practice, Fixed Carbon or FC derived by subtracting from 100 the value of moisture, volatile matter and ash.

$$\% FC = 100 - \%(\text{Moisture} + VM + \text{ash})$$

Significance of Various Parameters in Proximate Analysis

(a) Fixed carbon (FC):

Fixed carbon is the solid fuel left in the furnace after volatile matter is distilled off. It consistsmostly of carbon but also contains some hydrogen, oxygen, sulphur and nitrogen not driven off with the gases. Fixed carbon gives a rough estimate of heating value of coal.

Greater is the % of FC, smaller is the % VM content in the coal.

(b) Volatile Matter (VM):

The volatile matter is an index of the volatille gases present in the fuel. Typical range of volatile matter is 20 to 30%.

Volatile Matter

• Small amount is required for easy ignition of coal, but having large percentage leads to increase in the flame height, burns with smoke and hence causes heat loss.

High VM content means a large proportion of which escapes unburnt

(c) Ash Content:

Ash is an impurity that will not burn. Typical range is 5 to 40%

Ash

• Reduces burning capacity/calorific value.

• Increases transporting, handling and storage costs.

• Affects combustion efficiency

• Causes clinkering

- Reduces Calorific value

(d) Moisture Content: Since it replaces combustible matter, it decreases the heat content per kg of coal. Typical range is 0.5 to 10%

Some moisture is required to reduce the fly-ash.

Moisture

• High moisture content in a fule lowers the effective calorific value of the coal.

Numerical (Proximate Analysis):

Exactly 2.5 g of coal was weighed into a silica crucible. After heating for 20 min at 110 ^{0}C, the residue weighed 1.925 g. The crucible was then covered with a vented lid and strongly heated for 7 min at 900-950 ^{0}C in a muffle furnace. The residue weighed 1.328 g. The residue was then heated without lid till complete combustion occurs. The residue weighed now 0.204g. Find the % Moisture, %VM, % ash and % Fixed C of the coal sample.

Solution:

1. **% Moisture** = (weight loss due to removal of moisture/Total weight of coal sample taken) x 100 = (2.5-1.925)/2.5 x 100 = (0.575/2.5) x 100 =23

2. **% VM** = (weight loss due to removal of VM/Total weight of coal sample taken) x 100 = (1.925-1.328)/2.5 x 100 = 23.88

3. **% ash:** (weight of final residue/Total weight of coal sample taken) x 100 = (0.204/2.5) x 100 = 8.16

4. **% Fixed Carbon:** % FC = 100 - %(Moisture + VM + Ash) = 100-(23+23.88+8.16) = 44.96

Battery

Battery is an electrochemical cell or a group of two or more cells connected in series which converts chemical energy into electrical energy. Examples: Nickel-Cadmium Ni-Cd cell; Lead-acid storage cell, Laclanche (Zn-C) cell, Li-ion battery, etc.

Characteristics of a good commercial battery

A good commercial battery should have:

- ✓ Low cost
- ✓ Light in weight
- ✓ Small in size (i.e., portability)
- ✓ High energy efficiency
- ✓ High cycle life
- ✓ Long shelf life
- ✓ Excellent tolerance to variation of temp., vibration, moisture, EM wave, etc.

Types of batteries

In general, there are two types of batteries are available in the market:

1. Primary or non-rechargeable battery
2. Secondary or rechargeable battery

Primary Battery: Here, cell reaction (i.e., a redox reaction) is not reversible. It is also known as dry cell. Example: Laclanche cell

Secondary Battery

Here, cell reaction can be reversed during charging by the supply of an external source. It is also known as reversible cell. Example: Lad-acid storage cell

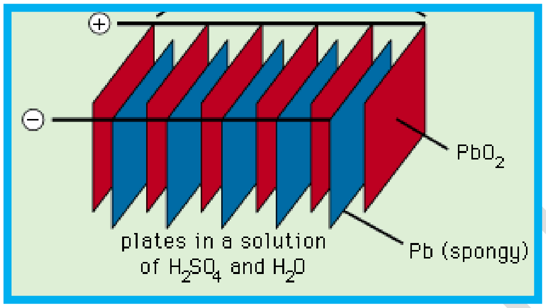
10.1 Lead-Acid Storage Cell-a rechargeable battery

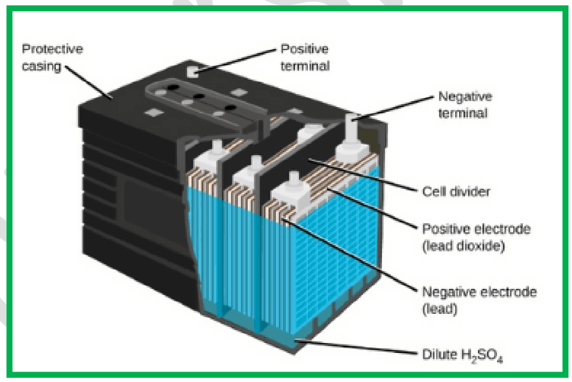
- ✓ It is a secondary cell which can operate both as a electrochemical cell and as a electrolytic cell. It is also known as lead-acid accumulator.
- ✓ It has the ability to supply electrical energy during discharging (i.e., acts as electrochemical cell).

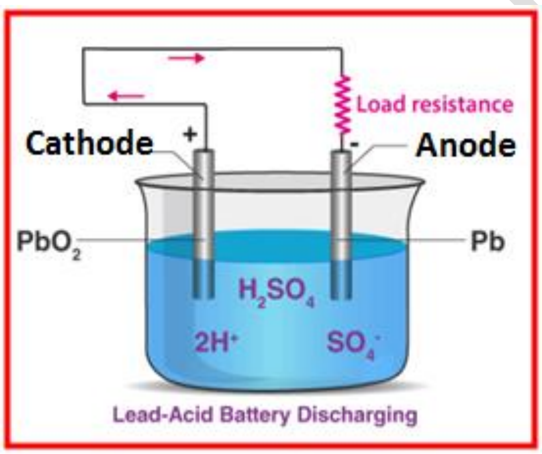
- ✓ Also, it has the ability to receive electrical energy during charging (i.e., acts as electrolytic cell)
- ✓ It can store a lot of charge and provide high current for short periods of time.
- ✓ The lead acid battery is packed in a thick rubber or plastic case to prevent leakage of the corrosive sulphuric acid.

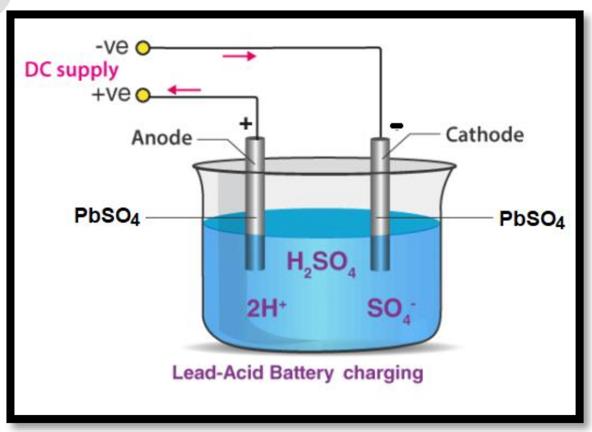
<u>Construction</u>

Like any electrochemical cell, it consists of an anode, a cathode and an electrolyte. Here, porous lead (Pb) acts as anode, lead coated with lead oxide (PbO_2) acts as cathode and 38% H_2SO_4 acts as electrolyte. In general, a storage cell consists of at least six numbers of such cells connected in series to provide a output voltage of ~12V.









<u>Working</u>

Its working consists of two processes: **A.**Discharging, and**B.**Charging

Discharging: It is said to be discharging when the battery is used for supplying electrical energy. The following reactions were occurring during discharging.

Chemical reactions for discharging:

Anode (Oxidation): $Pb + SO_4^{2-} \rightarrow PbSO_4\ (s) + 2e$ -------------- (1)

(Here, Pb(0) is oxidized to Pb^{2+})

Cathode (Reduction): $PbO_2 + 4H+ + SO_4^{2-} + 2e \rightarrow PbSO_4\ (s) + 2H_2O$ -------- (2)

(Here, Pb^{4+} is reduced to Pb^{2+})

Net cell reaction during discharging (a redox reaction): (1) + (2)

$Pb + PbO_2 + 4H+ + 2SO_4^{2-} \rightarrow 2PbSO_4\ (s) + 2H_2O + Energy$

Or $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4\ (s) + 2H_2O + Energy$

- ✓ In the discharged state, both the positive and negative plates become lead(II) sulfate ($PbSO_4$). The electrolyte loses much of its dissolved sulfuric acid and becomes primarily water.

Charging:

During discharging, the lead (Pb) of the anode and lead dioxide (PbO_2) of the cathode are covered with lead sulphate ($PbSO_4$).This causes the cell stop working after discharging for some period of time. For further use, it needs to be recharged by passing an external source greater than 2 Volt. This external source causes reversing the cell reactions taking place during discharging.

The following reactions were occurring during discharging.

Chemical reactions for charging:

Oxidation: $PbSO_4\ (s) + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e$ -------- (1)

(Here, Pb^{2+} is reduced to Pb^{4+})

Reduction:

$PbSO_4\ (s) + 2e \rightarrow Pb + SO_4^{2-}$ -------------- (2)

(Here, Pb^{2+} is reduced to Pb(0))

Net cell reaction during charging (a redox reaction): (1) + (2)

$2PbSO_4$ (s) + $2H_2O$ + Energy → Pb + PbO_2 + $4H^+$ + $2SO_4^{2-}$

Or $2PbSO_4$ (s) + $2H_2O$ + **External source** → Pb + PbO_2 + $2H_2SO_4$

*** Notice how the charging reaction is the exact opposite of the discharge reaction.

Applications: This cell is used in electrical vehicles, hospitals, trucks, buses, telephone exchange, inverter, UPS, etc.

Limitations:

- ✓ Excessive charging may damage the electrodes
- ✓ Excessive charging may leads to explosion of battery
- ✓ Lead metal is toxic in nature
- ✓ In cold weather, there is a decrease in output voltage.

Q. Write the chemical reactions occur during the discharging.

Q. Write the chemical reactions occur during the charging.

Q. What is an accumulator?

Q. Mention some limitations of lead-acid storage battery.

Q. What do you mean by charging?

Q. What do you mean by discharging?

Q. Briefly discuss the construction and working of lead-acid storage cell. (7 marks)

Q. Write the discharging and charging reaction of lead-acid battery. [3 marks]

Give Reason:

1. Why excessive charging is unwanted?

2. Output voltage of the battery decreases in cold weather.

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Fuel cell

- A fuel cell can be defined as an electrochemical cell that generates electrical energy from fuel via an electrochemical reaction.
- These cells require a continuous input of fuel and an oxidizing agent (generally oxygen) in order to continue the reactions that generate the electricity.
- Fuel cells can produce electricity continuously for as long as fuel and oxygen are supplied.
- A fuel cell is similar to electrochemical cells, which consist of a cathode, an anode, and an electrolyte that allows ions.
- The first fuel cells were invented by Sir William Grove in 1838. The first commercial use of fuel cells came more than a century later following the invention of the hydrogen–oxygen fuel cell by Francis Thomas Bacon in 1932. The alkaline fuel cell, also known as the Bacon fuel cell after its inventor, has been used in NASA space programs since the mid-1960s to generate power for satellites and space capsules.

Examples: H_2-O_2 fuel cell, propane-O_2 fuel cell, methanol-O_2 fuel cell, etc.

Hydrogen-Oxygen (H_2-O_2) fuel cell

- *Alkaline fuel cell or Hydrogen-oxygen fuel cell* was designed and first demonstrated publicly by *Francis Thomas Bacon* in 1959. It was used as a primary source of electrical energy in the Apollo space program.
- The cell consists of two inert porous carbon electrodes impregnated with a suitable catalyst such as Pt, Ag, etc. Here, catalyst is used to increase the rate of reaction.
- The space between the two electrodes is filled with a concentrated solution of KOH or NaOH which serves as an electrolyte.
- H_2 gas and O_2 gas are bubbled into the electrolyte through the porous carbon electrodes. Thus the overall reaction involves the combination of hydrogen gas and oxygen gas to form water.
- The cell runs continuously until the reactant's supply is exhausted. They do not store chemical energy.

- This type of cell operates efficiently in the temperature range 343–413 K (70-140 ^{0}C) and provides a potential of about 0.9 V.
- Efficiency is about 70%.

The following chemical reactions are occurring during its working process:

Anode: $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e$ -------- (1)

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

Net cell reaction: (Eq. 1. + Eq. 2) $2H_{2(g)} + O_{2(g)} \rightarrow 2\,H_2O_{(l)} + 1.23$ V

- One such cell can generate power of about 1 V, far from enough to power a vehicle.
- In actual practice, a large number of such cells are stacked together in series to make a battery. Cell output ranges from 300 W to 5000 W.

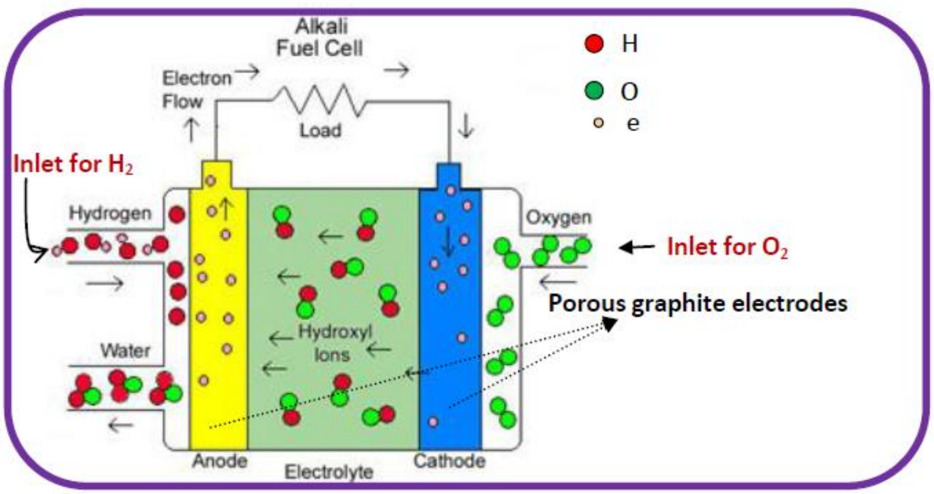

Fig. H_2-O_2 fuel cell

Advantages:

- Energy conversion is high (75-80%).
- Produces water of potable quality.
- Noise and thermal pollution are low.
- Used in space applications and remote areas.
- Saves fossil fuels.

Limitations:

- High cost
- Pure hydrogen is also costly.
- Finding a suitable catalyst for electrode is a tough task.
- H_2 and O_2 cylinder to be carried along with the battery.

Applications: Some of the applications are listed below:

- Fuel cell electric vehicles(FCEVs) use clean fuels and are therefore more eco-friendly than internal combustion engine-based vehicles.
- They have been used to power many space expeditions including the Appolo space program.
- Generally, the by-product produced from these cells ispure water.
- The portability of some fuel cells is extremely useful in some military applications.
- These electrochemical cells can also be used to power several electronic devices.
- Used in military vehicles, aircrafts, etc.
- Fuel cells are also used as primary or backup sources of electricity in many remote areas.

Q.What is a fuel cell? Give an example.

Ans. A fuel cell can be defined as an electrochemical cell that generates electrical energy from fuel via an electrochemical reaction. Example: H_2-O_2 fuel cell

Q. Mention some limitations of a fuel cell.

Q. Mention some advantages of a fuel cell.

Q. Write the chemical reactions involved during the working of a H_2-O_2fuel cell.

Q. Discuss the construction and working of a H_2-O_2 fuel cell. (7 marks)

Lithium Ion Battery

Lithium-ion batteries are rechargeable cell that stores energy by using a special process called **intercalation/de-intercalation**. *Intercalation* is the insertion of an ion into layered materials (e.g. graphite, MoS_2, etc.) with layered structures and de-intercalation means extraction of ions from the layered materials.

It works by moving lithium ions between the positive and negative electrodes during charging and discharging. This movement of ions allows the battery to store and release electrical energy.

Construction:

Lithium ion battery is made up of one or more cells and each cell has the following essential components, namely- **an anode, a cathode, a separator, an electrolyte and two current collectors (positive and negative).**

- The positive electrode is made of Lithium doped cobalt oxide ($LiCoO_2$). The negative electrode is made up of carbon (graphite).
- The electrolyte is a lithium salt in an organic solvent i.e. Lithium hexafluorophosphate. ($LiPF_6$)

  N.B.: Lithium reacts vigorously with water to form lithium hydroxide (LiOH) and hydrogen gas. Thus, a non-aqueous electrolyte is typically used, and a sealed container rigidly excludes moisture from the battery pack.
- The negative electrode and the positive electrode are prevented from shorting by a separator (a semipermeable membrane).
- The electrolyte carries positively charged lithium ions from the anode to the cathode and vice versa through the separator.
- The negative and positive electrodes swap their electrochemical roles (anode and cathode) when the cell is charged.
- Lithium-Ion batteries have a nominal voltage of 3.7 volts per cell.

Working:
During discharging it supplies electrical energy.

(A) Discharging: (Converts Chemical energy to electrical enegy)

- During discharging electrons flow from the anode to the cathode through the external circuit.
- An oxidation half-reaction at the anode produces positively charged lithium ions and negatively charged electrons.
- Lithium ions move through the electrolyte; electrons move through the external circuit toward the cathode where they recombine with the cathode material in a reduction half-reaction.
- The electrolyte provides a conductive medium for lithium ions but does not participate in the electrochemical reaction.

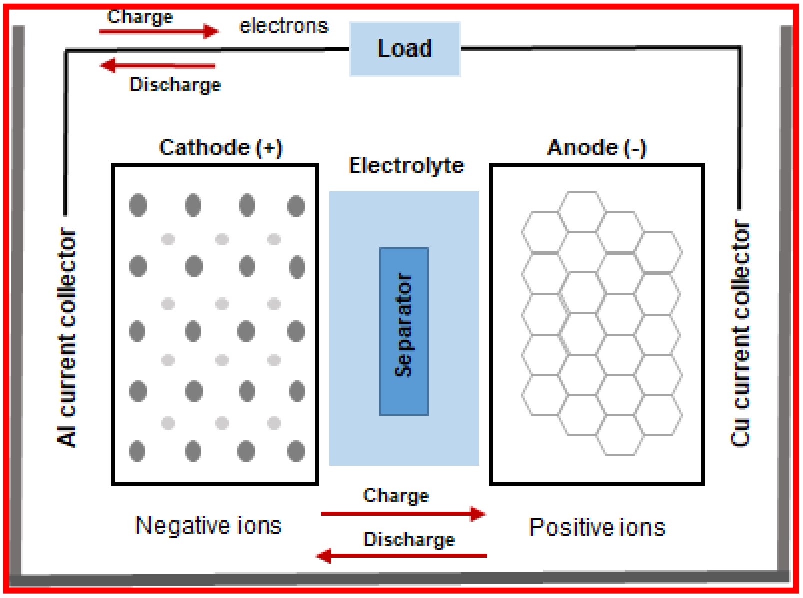

Fig. A schematic diagram showing how a lithium-ion battery works

Discharging Reactions:

During the discharging of the battery, the anode releases lithium ions to the cathode, which generates an electron flow from one side to the other, and during this process, an electric current is provided.

The opposite happens when a device is connected to an extrenal source and the lithium ions are released by the cathode and received by the anode; this is precisely how a lithium ion battery works.

- The negative electrode half-reaction for the lithiated graphite (LiC_6)is:

- **At Anode: $LiC_6 \rightleftharpoons C_6 + Li^+ + e$**
- The positive electrode half-reaction in the lithium-doped cobalt oxide substrate is:

- At cathode: **$CoO_2 + Li^+ + e \rightleftharpoons LiCoO_2$**

  Net cell reaction: $LiC_6 + CoO_2 \rightleftharpoons C_6 + LiCoO_2$

- Generates 11.6 kWh per kilogram of lithium

(B) Charging: (Converts electrical energy to chemical energy)

During charging these reactions and transports go in the opposite direction: electrons move from the positive electrode to the negative electrode through the external circuit. To charge the cell the external circuit has to provide electrical energy. This energy is then stored as chemical energy in the cell.

Both electrodes allow lithium ions to move in and out of their structures with a process called *insertion* (*intercalation*) or *extraction* (*deintercalation*), respectively.

Advantages:

- **High specific Energy Density:** (Energy density is measured in watt-hours per kilogram (Wh/kg) and it is the amount of energy the battery can store with respect to its mass)
- **High specific Power density:** Power density is measured in watts per kilogram (W/kg) and is the amount of power that can be generated by the battery with respect to its mass.
- **Low *Self-discharge rate and high life span***
- ***Low maintenance***
- ***High Cell voltage:*** The voltage produced by each lithium ion cell is about 3.6 volt, constant supply of power a longer lifespan Available in Various Sizes
- ***Compact in size and light in weight***
- ***Fast charging rate***
- ***No liquid electrolyte is used***

Limitations:

Costly, chances of fire hazard, has d**isposal and recycling issue**

- The mining process of lithium metal produces a lot of greenhouse gases, which causes the depletion of the ozone layer.
- The extraction process of lithium is a highly water-intensive proces
- Relatively expensive

Uses: Lithium ion batteries are used in a multitude of applications from consumer electronics, toys, power tools, electric vehicle, in solar and wind power storage, in aerospace technology owing to its light weight, in medical devices (pacemakers), etc.

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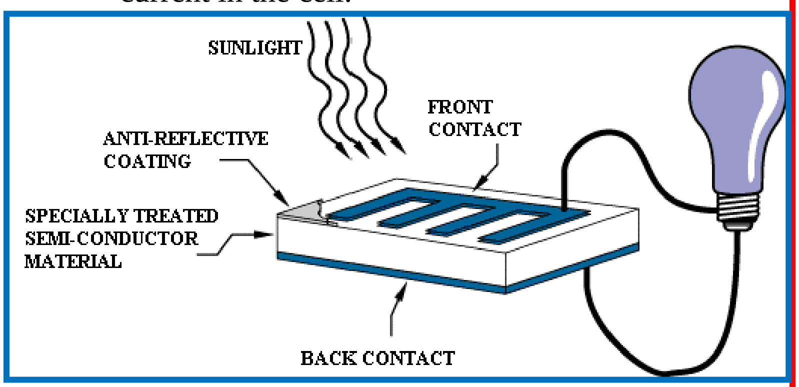
PV Cells/Solar Cells

Photovoltaic (PV) materials and devices converts the Sun's energy into useful electricity through a process called the photovoltaic effect. The **photovoltaic effect** is a process that generates voltage or electric current in a photovoltaic cell when it is exposed to sunlight.

Solar cells are composed of two different types of semiconductors—a p-type and an n-type—that are joined together to create a **p-n junction**. By joining these two types of semiconductors, an electric field is formed in the region of the junction as electrons move to the positive p-side and holes move to the negative n-side. This field causes negatively charged particles to move in one direction and positively charged particles in the other direction. Light is composed of photons, which are simply small bundles of electromagnetic radiation or energy. When light of a suitable wavelength is incident on these cells, energy from the photon is transferred to an electron of the semiconducting material, causing it to jump to a higher energy state known as the conduction band. In their excited state in the conduction band, these electrons are free to move through the material, and it is this motion of the electron that creates an electric current in the cell.



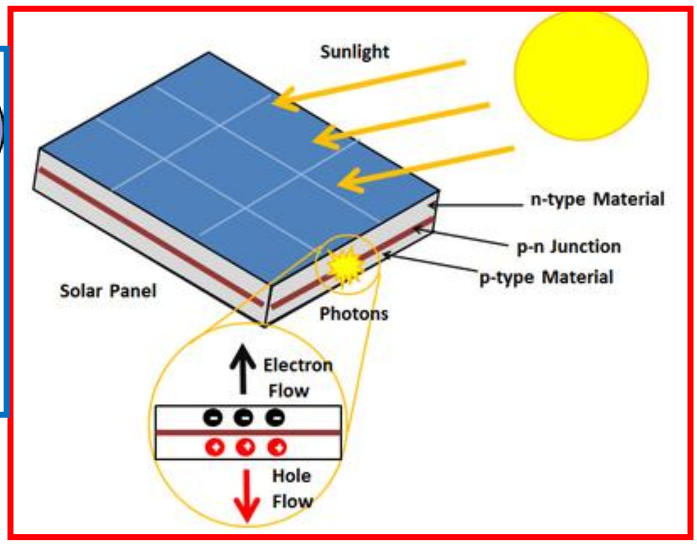


Fig. A diagram showing the photovoltaic effect

The steps involved in solar cells include:

- **Light absorption**: Light is absorbed by the solar cell, knocking electrons loose.
- **Electron flow**: The loose electrons flow, creating an electrical current.
- **Electrical current capture**: The electrical current is captured and transferred to wires.

PV materials: Silicon, Cadmium telluride (CdTe), Gallium Arsenide (GaAs), Copper indium gallium diselenide (CIGS), Fullerene (C_{60}).

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