# ENGINEERING CHEMISTRY

## UNIT-IV

## Chemistry of Energy Devices

# SYLLABUS

Unit-4

**Chemistry of Energy Devices**

- Introduction to Energy storage and conversion devices, Principles and applications of Batteries, Fuel Cells and Supercapacitors; Photocatalytic hydrogen production; Traditional and new generation solar cells

| **Part-1** | **Part-2** |
| --- | --- |
| Principles and applications of Batteries, Fuel Cells and Supercapacitors | Photocatalytic hydrogen production; Traditional and new generation solar cells |

# Energy

According to the **law of conservation of energy**, **it can neither be created nor be destroyed, it can only be changed from one form to another.**

Thus, we cannot produce energy to do certain work. Therefore, we use certain substances which help us transform one form of energy to another form.

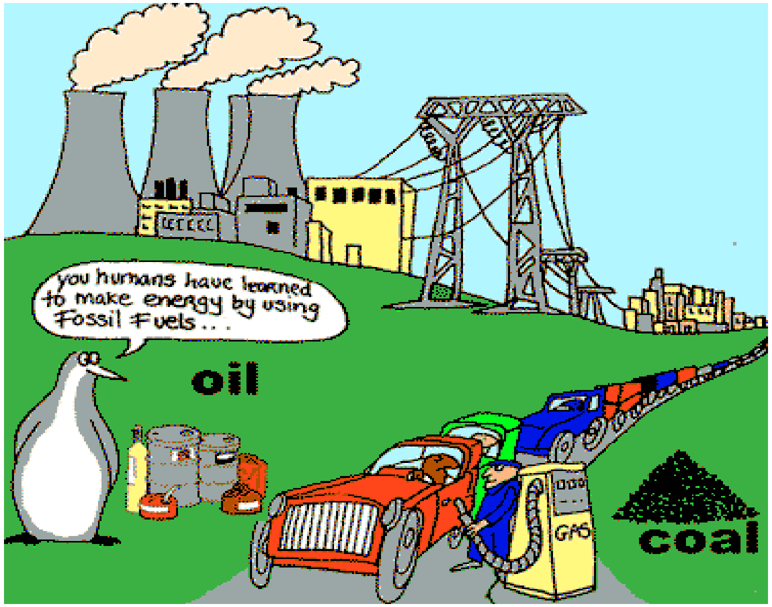
For example, when we **burn paper with a matchstick**, light is produced by the flame.

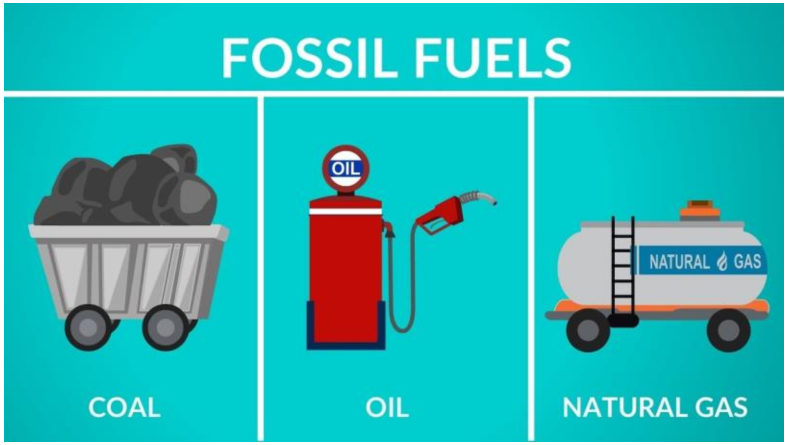

If we analyze this closely, **light energy is not created over there**, it has just been produced due to the **transformation** of heat energy provided by the matchstick into light energy .

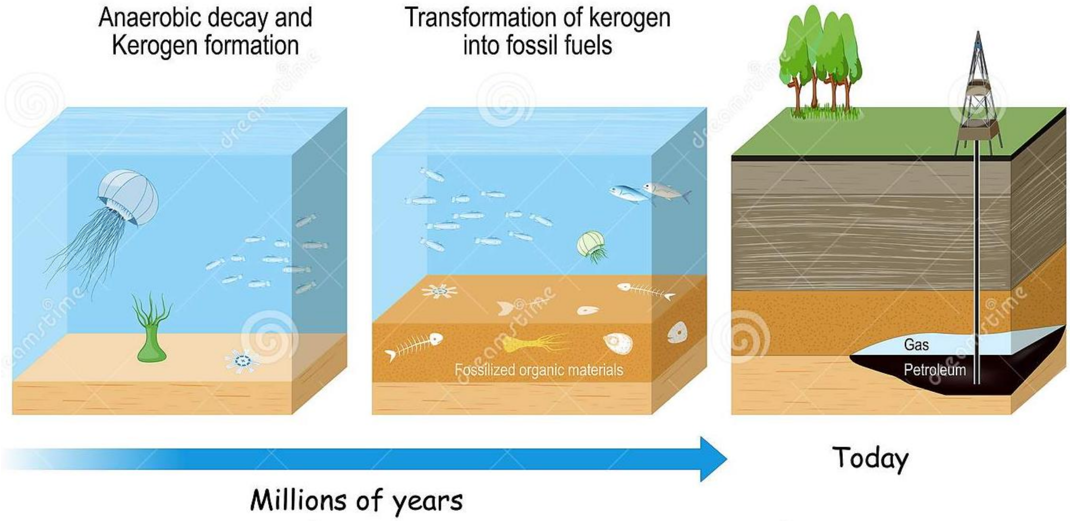
Thus, we always need a certain substance to convert one form of energy into another for accomplishing various jobs. **We call such materials as fuels.** In other words, any substance which upon combustion produces a usable amount of energy is known as **fuel**. Example: fossil fuels, biogas, nuclear energy, etc.

# Energy

- **Renewable source of energy:** one which is **inexhaustible**. *Example:* Solar energy.
- **Non-renewable source of energy:** one which is **exhaustible**. *Example:* Fossil Fuels.



# Energy

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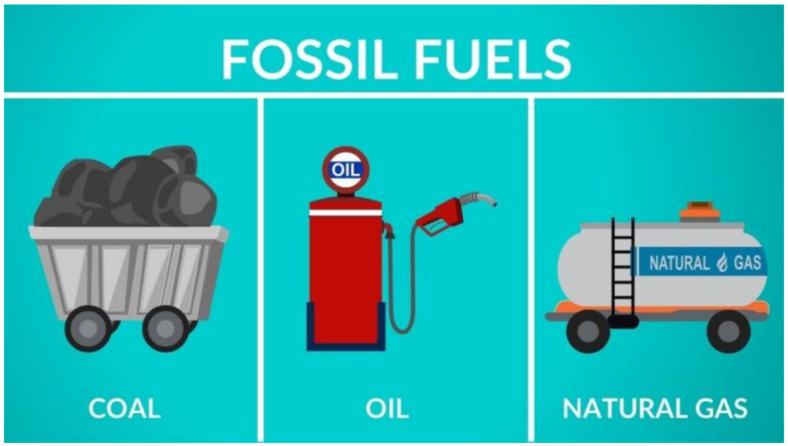
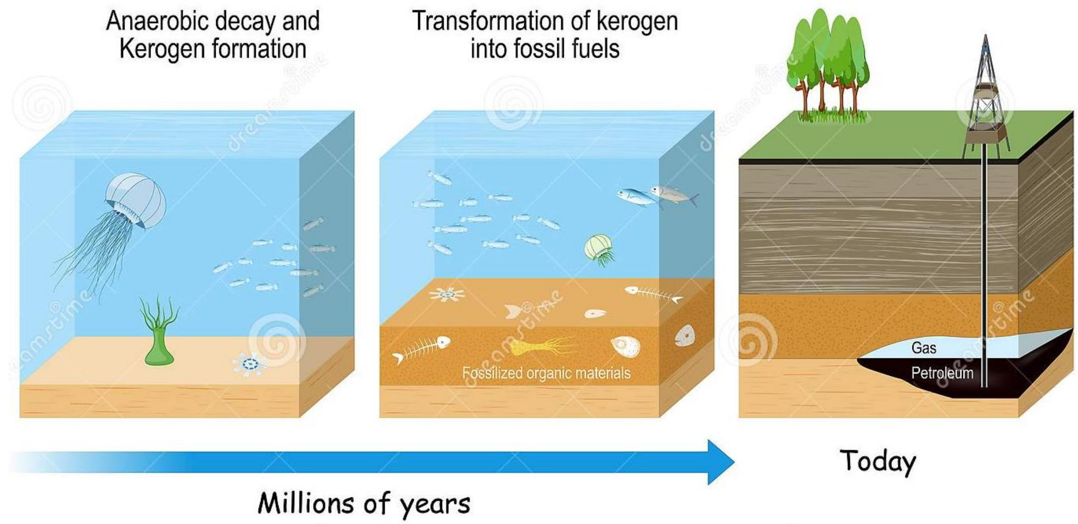
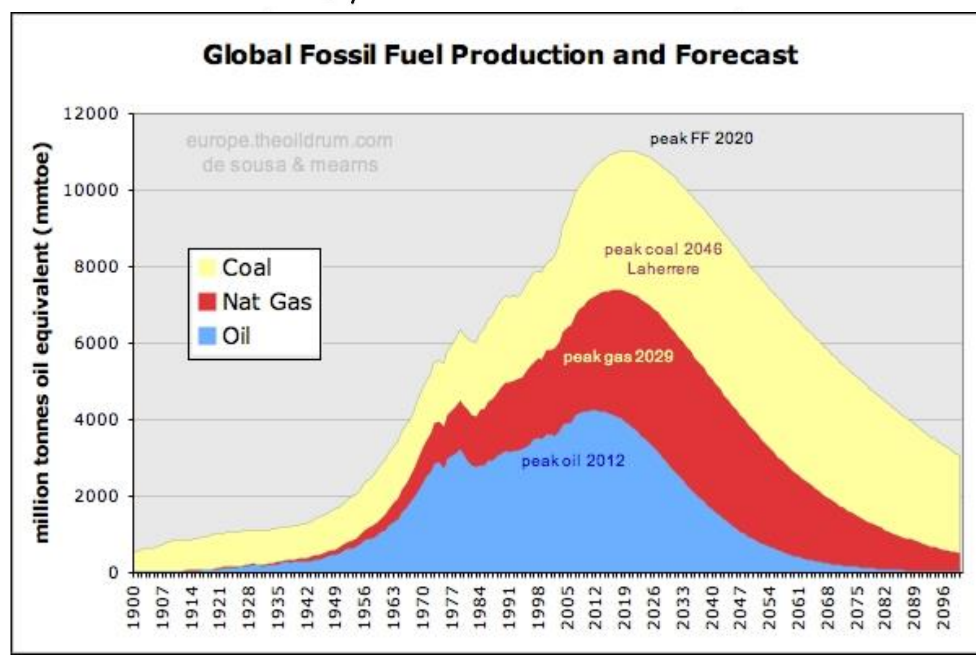



**Fossil fuels** are made from decomposing plants and animals. These **fuels** are found in the Earth's crust and contain carbon and hydrogen, which can be burned for energy. Coal, oil, and natural **gas** are examples of **fossil fuels**

**Fossil fuel depletion** is the extraction of natural gas, oil and coal reserves at a ra te higher than nature stock up them.



# Fossil Fuels

Fossil fuels are the **dead and decayed remains of plants and animals** subjected to decades of pressure and temperature under the earth's crust.

Primarily fossil fuels are hydrocarbons. They are convenient and effective. They provide the calorific value required to fulfil our needs. Even though they are available in plenty right now, they are a non-renewable source of energy.

The burning of fossil fuels is responsible for a large section of the world's pollution index.

**Types of fossil fuels:**

Coal
Oil
Natural Gas

# Alternate Energy Sources

## Energy Storage and Conversion Devices:

**Energy storage and conversion is vital component of our energy system.**
**Five technical devices that can be used to convert or store energy**

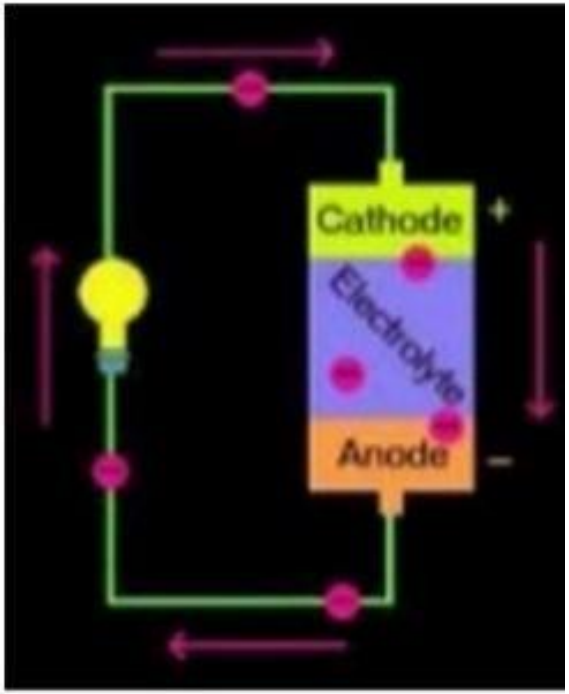
1. Batteries
2. Fuel Cell
3. Supercapacitors
4. Photo-voltaic (Solar Cell)
5. Water splitting

# Batteries

Convert stored chemical energy into electrical energy

# Batteries

- Convert stored chemical energy into electrical energy
- Reaction between chemicals take place
- Consisting of electrochemical cells
- Contains
  - Electrodes
  - Electrolyte




SAMSUNG 삼성SDI

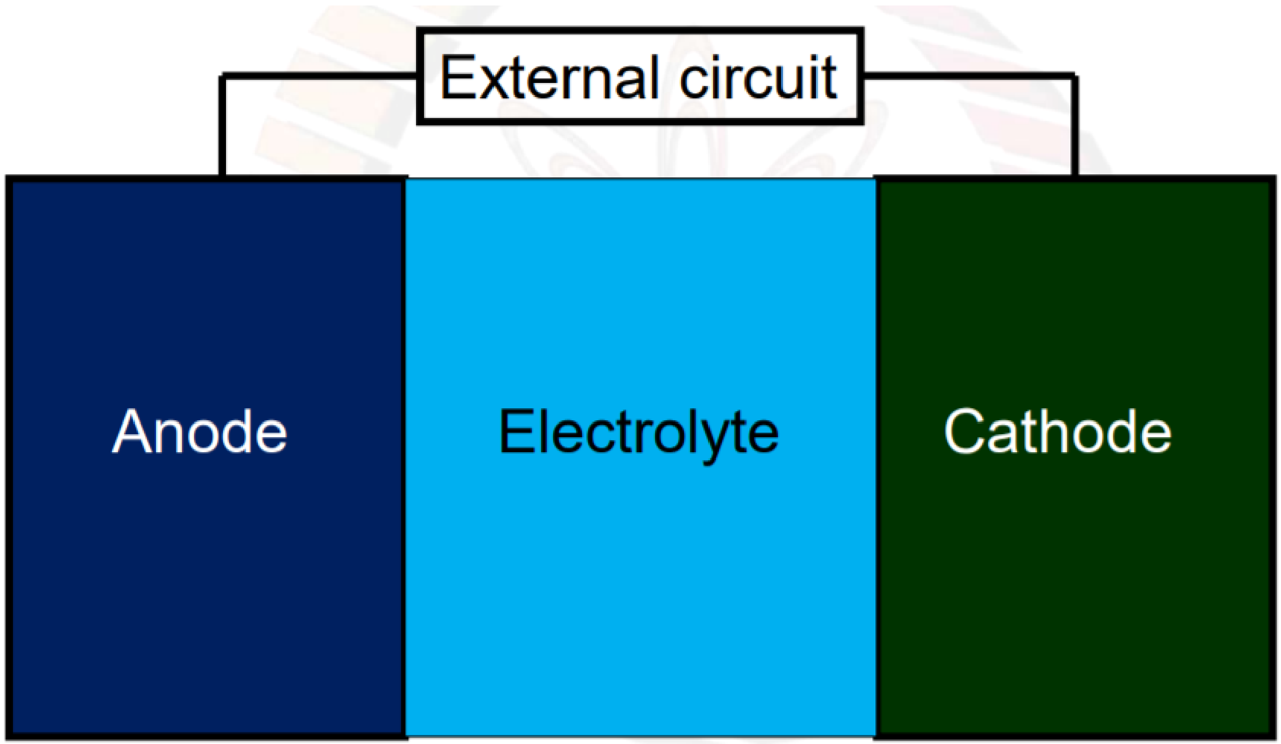
Panasonic ideas for life

SANYO

LG화학

SONY

# Construction




| | | |
|---|---|---|
| **Anode** | **Oxidation** | **Loss of electrons** |
| **Cathode** | **Reduction** | **Gain of electrons** |

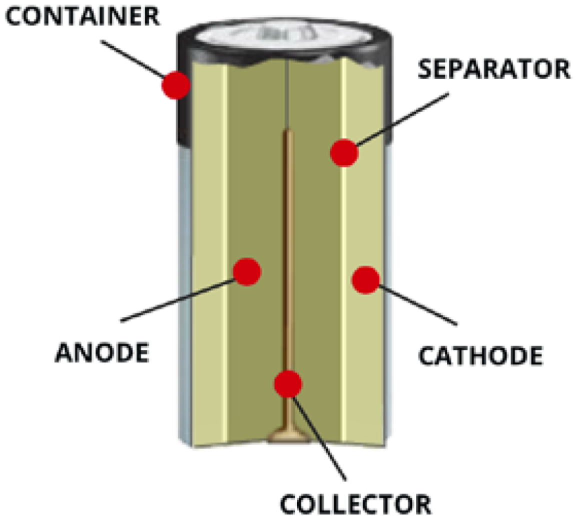
# Construction

Battery has a metal or a plastic case and inside it, cathode, anode and electrolytes are pre sent.

Separator creates barrier between the cathode and anode.

Current collector brass pin is present in the middle of the cell conducts electricity to outsi de circuit.

The total energy contained within a battery can be described using Amp-hours. Example, battery that can provide 4 A-hrs can generate 4 A for 1 hour, 2 A for 2 hrs., etc.



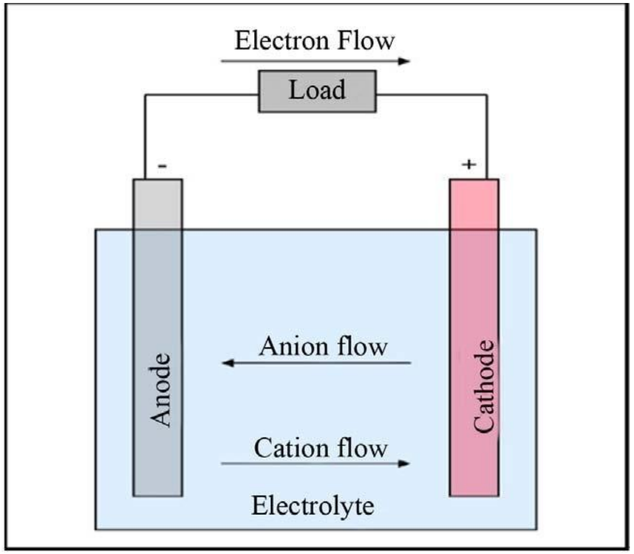
# Working

Both electrodes slowly dissolve in the acid:

• At the anode, electrons are used in chemical reactions as the metal dissolves

• At the cathode, electrons are absorbed into th e electrode as the metal dissolves

• The net result is a buildup of electrons at the cathode

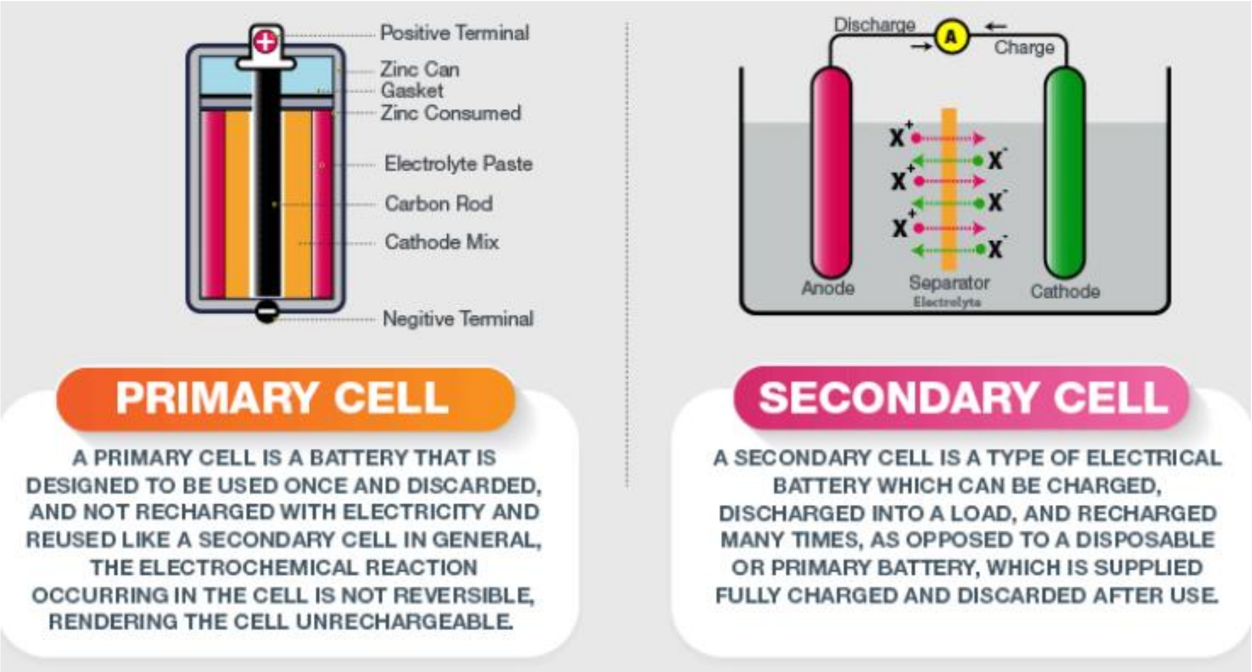


# Types

Battery or cells are referred to as the parallel combination of electrochemical cells.

There are two types of cells:
Primary Cell
Secondary Cell

The major difference between a primary cell and the secondary cell is that primary cells are the ones that cannot be charged but secondary cells are the ones that are rechargeable.



# Types

**Primary cell:**

Primary cells have high density and get discharged slowly. Since there is no fluid inside these cells they are also known as dry cells. The internal resistance is high and the chemical reaction is irreversible. Its initial cost is cheap and also primary cells are easy to use.

**Secondary cell:**

Secondary cells have low energy density and are made of various nanomaterials and wet cells. The internal resistance is low and the chemical reaction is reversible. Its initial cost is high and is a little complicated to use when compared to the primary cell.

# Difference

Primary cells are the ones which cannot be recharged and have to be discarded after the expiration of the lifetime whereas, secondary cells need to be recharged when the charge gets over. Both the types of battery are used extensively in various appliances and these cells differ in size and material used in them.

### Difference Between Primary Cell and Secondary Cell

| Primary Cell | Secondary Cell |
|---|---|
| Have high energy density and slow in discharge and easy to use | They are smaller energy density |
| There are no fluids in the cells hence it is also called as dry cells | There are made up of wet cells (flooded and liquid cells) and molten salt (liquid cells with different composition) |
| It has high internal resistance | It has a low internal resistance |
| It has an irreversible chemical reaction | It has a reversible chemical reaction |
| Its design is smaller and lighter | Its design is more complex and heavier |
| Its initial cost is cheap | Its initial cost is high |

# Primary Cells

$$2NH_4(aq) + 2e^- \rightarrow 2NH_3(g) + H_2(g)$$

The manganese(IV) oxide in the cell removes the hydrogen produced by the ammonium chloride, according to the following reaction:

$$2MnO_2(s) + H_2(g) \rightarrow Mn_2O_3(s) + H_2O(l)$$

The combined result of these two reactions takes place at the cathode. Adding these two reactions together, we get:

$$2NH_4(aq) + 2MnO_2(s) + 2e^{\rightarrow} Mn_2O_3(s) + 2NH_3(g) + H_2O(l)$$

Finally, the anode half-reaction is as follows:

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

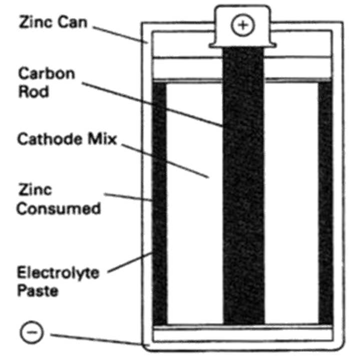
Therefore, the overall equation for the cell is:

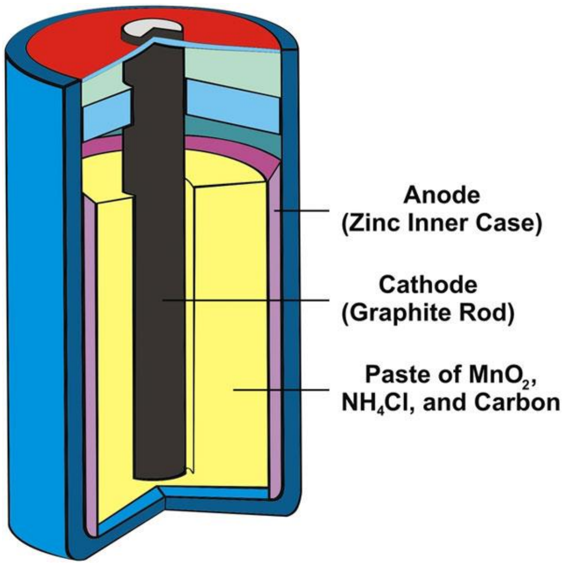
$$Zn(s) + 2MnO_2(s) + 2NH_4(aq) \rightarrow Mn_2O_3(s) + H_2O(l) + Zn_2 + 2NH_3(g)$$

Primary cells are: Zinc-Carbon cell, Alkaline cell, Button cell etc…

## Zinc-Carbon BATTERIES

$2MnO_2 + 2NH_4Cl + Zn$ --> $ZnCL_2 \cdot 2NH_3 + H_2O + MN_2O_3$



# Difference

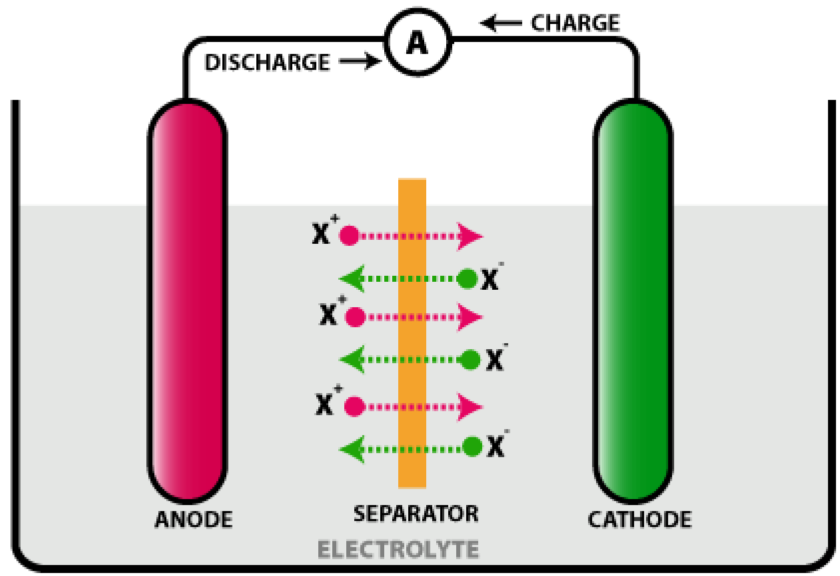
- Alkaline Battery
- Zinc powered, basic electrolyte
- Higher energy density
- Functioning with a more stable chemistry
- Shelf-life: 8 years because of zinc powder
- Long lifetime both on the shelf and better performance
- Can power all devices high and low drains
- Use:

  Digital camera, game console, remotes

- Zinc-Carbon Battery
- Zinc body, acidic electrolyte
- Case is part of the anode
- Zinc casing slowly eaten away by the acidic electrolyte
- Cheaper then Alkaline
- Shelf-life: 1-3 years because of metal body
- Intended for low-drain devices
- Use:

  Kid toys, radios, alarm clocks

# Secondary Cells




**Secondary cell:**

- Rechargeable batteries
- Reaction can be readily reversed
- Similar to primary cells except redox reaction can be reversed
- Recharging:
  - Electrodes undergo the opposite process than discharging
  - Cathode is oxidized and produces electrons
  - Electrons absorbed by anode

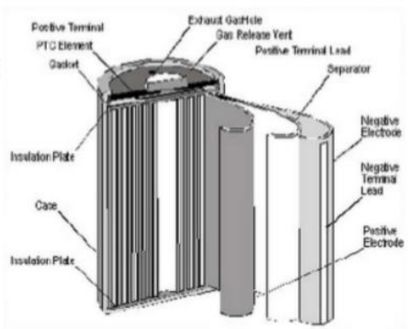
# Secondary Cells

Secondary cells are: Nickel-Cadmium batter, Lead-Acid battery, Lithium ion battery

Anode: Cadmium hydroxide, $Cd(OH)_2$

Cathode: Nickel hydroxide, $Ni(OH)_2$

Electrolyte: Potassium hydroxide, KOH




The half-reactions are:

$Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$

$2NiO(OH) + Cd + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$

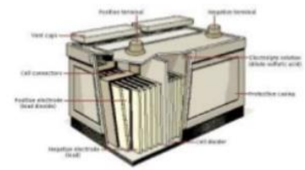
Overall reaction:

$2NiO(OH) + Cd + 2H_2O \rightarrow 2Ni(OH)_2 + Cd(OH)_2$

Anode: Porous lead

Cathode: Lead-dioxide

Electrolyte: Sulfuric acid, 6 molar $H_2SO_4$



Discharging

(+) electrode: PbO2(s) + 4H+(aq) + SO42-(aq) + 2e- → PbSO4(s) + 2H2O(l)

(-) electrode: Pb(s) + SO42-(aq) → PbSO4(s) + 2e-

During charging

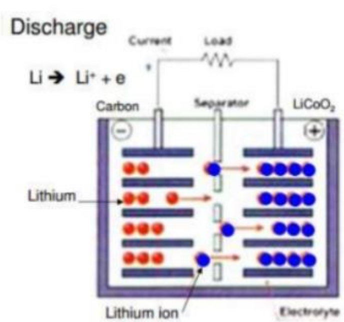
(+) electrode: PbSO4(s) + 2H2O(l) → PbO2(s) + 4H+(aq) + SO42-(aq) + 2e-

(-) electrode: PbSO4(s) + 2e- → Pb(s) + SO42-(aq)

Anode: Graphite

Cathode: Lithium manganese dioxide

Electrolyte: mixture of lithium salts




Lithium ion battery half cell reactions

$CoO_2 + Li^+ + e^- \leftrightarrow LiCoO_2\ E^\circ = 1V$

$Li^+ + C_6 + e^- \leftrightarrow LiC6\ E^\circ \sim -3V$

Overall reaction during discharge

$CoO_2 + LiC_6 \leftrightarrow LiCoO_2 + C_6$

$E_{oc} = E^+ - E^- = 1 - (-3.01) = 4V$

# Types of Secondary Cells

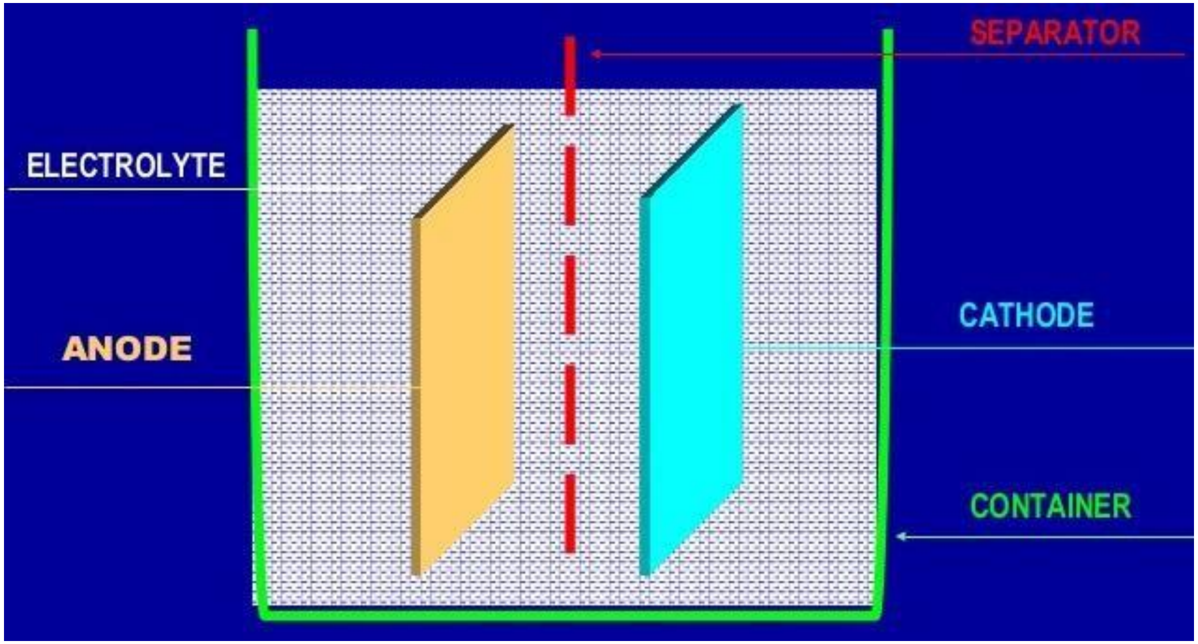
1. Lead-Acid battery (Pb/H+)
2. Nickel-Cadamium Battery (Ni-Cd)
3. Nickel-Iron Battery (Ni-Fe)
4. Nickel-Metal Hydride battery (Ni-MH)
5. Nickel-Zinc Batteries (Ni-Zn)
6. Lithium-Ion Battery ($C\text{-}LiM_xO_y$)
7. Lithium-Polymer Battery ($C\text{-}LiM_xO_y$)

# Lithium-Ion Battery

- The name "Lithium Ion Battery (LIB)" was given by **T. Nagaura** and **K. Tozawa**
- And the concept of LIBs was firstly introduced by **Asahi Kasei Co. Ltd.**
- LIBs was first proposed by **M. S. Whittingham** in the 1970s, **$TiS_2$** was used as th e **cathode** and **Lithium metal** as **Anode**
- Li is lightest metal and has one of highest standard reduction potentials (-3.0 V)
- Theoretical specific capacity of 3860 Ah/Kg in comparison with 820 Ah/kg for Zn
- Theoretical capacity can be calculated by Faraday's law:
  - $Q_{theoretical}$ = (nF) / (3600*Mw) mAh g-1.

  Where n is the number of charge carrier, F is the Faraday constant and Mw is the molecular weight of the active material used in the electrode.
- First commercial LIBs was released by Sony in 1991
- Battery performance is related not only to capacity but also how fast current can b e drawn from it:
  - Specific energy (Wh/Kg), Energy Density (Wh/$cm^3$) and power density (W/K g)

# Lithium-Ion Battery




- Cathode
  - Positive terminal
  - Chemical reduction occurs (gain electrons)
- Anode
  - Negative terminal
  - Chemical oxidation occurs (lose electrons)
- Electrolytes allow:
  - Separation of ionic transport and electrical transport
  - Ions to move between electrodes and terminals
  - Current to flow out of the battery to perform work

**ANODE REACTION:** is an oxidation reaction which releases electrons (Anode is the –ve electrode in EC cell)

**CATHODE REACTION:** is a reduction reaction which consumes electrons (Cathode is the +ve electrode in EC cell)

**ELECTROLYTE** is an ion-conducting medium which conducts ions between the electrodes so that the above reactions can take place

# Capacitor

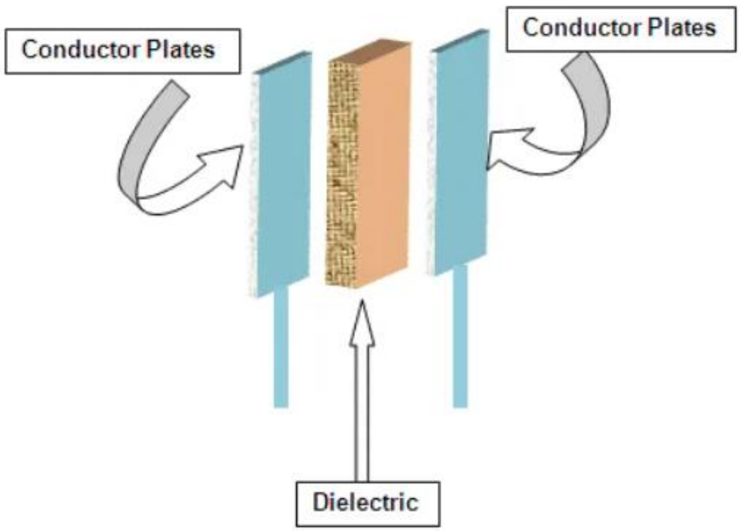
Let's first take a look at the working of a typical capacitor.

Standard capacitors are made of two metallic plates or electrodes that separate a dielectri c substance between them. Upon the application of voltage, electrons accumulate at one of the electrodes, thereby storing the electrical charge.

Meanwhile, the dielectric material that is wedged between the electrodes undergoes a pro cess called "dielectric polarization" and helps to increase the capacitance.

**Dielectric Polarization-** When an electric field is applie d to a capacitor, the dielectric material (or electric insula tor- Ceramic, glass, and mica) become polarized, the ne gative charges in the material orient themselves toward t he positive electrode and the positive charges shift towar d the negative electrode

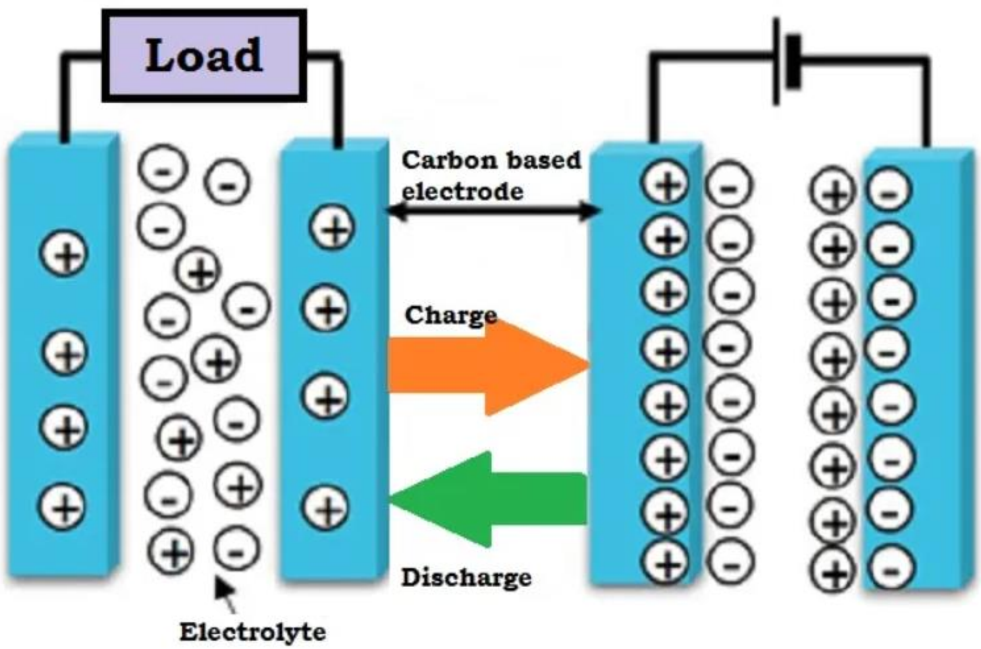
A dielectric material is a poor conductor of electricity bu t an efficient supporter of electrostatic fields.



# Supercapacitor

Supercapacitor also work on the same principle except that the wedging material is an ele ctrolytic solution rather than a dielectric substance. Upon voltage application, an “electri cal double layer” will be created that aligns both negative and positive charges along the boundaries of electrodes and the electrolytic solution.

This place acts as a warehouse for storing electric charges. Activated carbon is often used to expand the boundary areas. This is because, the supercapacitor’s capacitance is in dire ct proportion to the area of “electrical double layer”. This activated carbon is a known po rous material and has many surface holes that help in covering a big surface area.

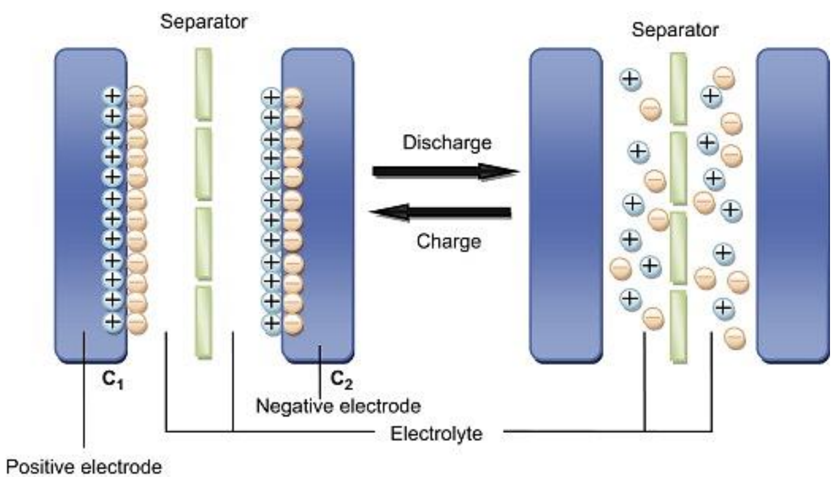


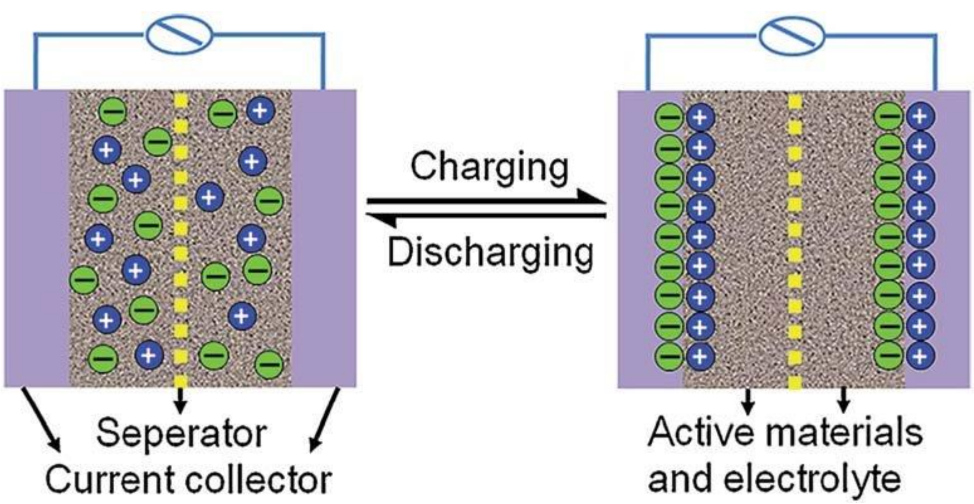
# Supercapacitor

Due to the electrolytic solution and electrodes, supercapacitors share the structure of a typical battery for electricity storage. While chemical reactions take place between the electrolytic solution and the electrodes in a battery, supercapacitors allow only electrons movement between electrodes. These differences result in varying properties between a battery and supercapacitor.

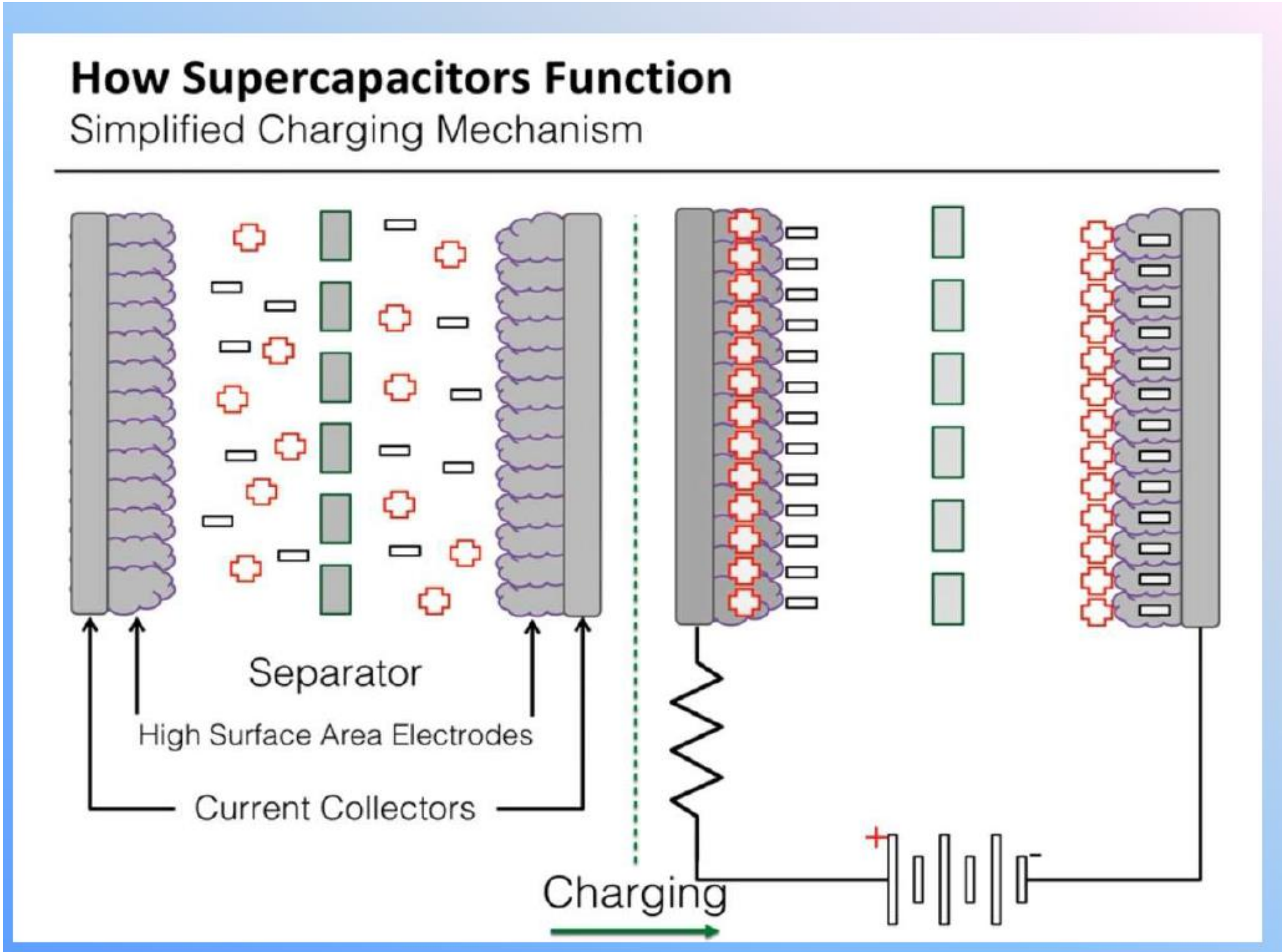
## ➢ *Supercapacitor*

- Supercapacitors (SCs) are electrochemical energy storage devices that store and release energy by reversible adsorption and desorption of ions at the interfaces between electrode materials and electrolytes
- In 1950s General Electric Enginners started experimenting components using porou electrdes for fuel cells and rechargeable batteries
- In 1957s H. Becker developed ‘Low voltage electrocatalytic capacitor with porous carbon electrodes
- That capacitor came to known as Supercapacitor as it stored very high amount of energy.



# ➢ *Supercapacitor*



# Types

As earlier mentioned, Supercapacitors make use of two basic principles for energy storage i.e. electrochemical pseudocapacitance and static double layered capacitance. Based on this, supercapacitors are categorized into three different types. They are:

Double Layered Capacitors
Pseudocapacitors
Hybrid Capacitors

**Double Layered Capacitors:**

In Double Layered Capacitors, Storage of electrical energy is achieved by charge separation in double layer. This acts as a boundary between the conductor electrode and electrolyte.

The electrodes are made from activated carbon or with derivatives that have greater electrostatic double layered capacitance than an electrochemical pseudocapacitance.

# Types

**Pseudocapacitors:**

They have polymer conducting electrodes or transistion metal oxides that possess large electrochemical pseudocapacitance.

Storage of electrical energy is an electrochemical process and is achieved through redox reactions, intercalation on electrode surface by ions that are specifically absorbed.

**Hybrid Capacitors:**

Here, the electrodes are asymmetric where one of the electrodes exhibit electrostatic property while the other exhibits electrochemical capacitance. Because both Pseudocapacitance and Double-Layered capacitance make inseparable contributions to the full capacitance of an electrochemical capacitor, the concept of Supercabattery and Supercapattery have been proposed. This helps in giving clarity on hybrid devices that act both like a battery and a supercapacitor.

# Advantages

**Long life-** Works for large number of cycle without wear and aging

**Rapid charging-** Takes a second to charge completely due to low internal resistance

**Low cost-** Less expensive as compared to electrochemical battery

**High power storage-** Stores huge amount of energy in a small volume, if large surface ar ea materials are used.

**Faster release-** Release the energy much faster than battery

# Disadvantages

**Limitations-** Self discharge, packing problem

**Low voltage –** Cells hold less voltage, serial connections are needed need

**Danger –** Due to rapid charge and discharge, have potential to be deadly to human

# Applications

Since supercapacitors are bridging the gap between capacitors and batteries, they are bei ng used in large number of applications, such as electrical vehicle to extend the life of ba tteries

Used as back up and UPS system

The automotive industry is making use of this approach by using electrical generators tha t change kinetic energy into electrical energy. This electrical energy is stored in supercap acitors and is later used to supply power required for acceleration

Functions well in low temperature, can give car a boost in cold weather when batteries ar e their worst

Low powered applications where quick recharge or high life cycle is important, make use of the supercapacitor technology. MP3 players, photographic flash, static memories are a few such applications.

# Fuel Cells

- A power generating device that converts chemical energy of fuel ($H_2$ or MeOH) and air ($O_2$) directly to electric energy by electrochemical reactions without combustion and moving parts.
- Operates likes a battery but does not run down or require recharging, produces energy in the form of electricity and heat as long as the fuel is supplied.
- An excellent alternative energy resource from environmental point of view. Since the fuel cells rely on chemistry and not combustion, they are inherently quiet, ultra clean and produces negligible emissions of pollutants.
- Fuel cells differ from conventional cells in the respect that active material (fuel & oxygen) are not contained within the cell but are supplied from outside.
- Despite being invented in the year 1838, fuel cells began commercial use only a century later when they were used by NASA to power space capsules and satellites.

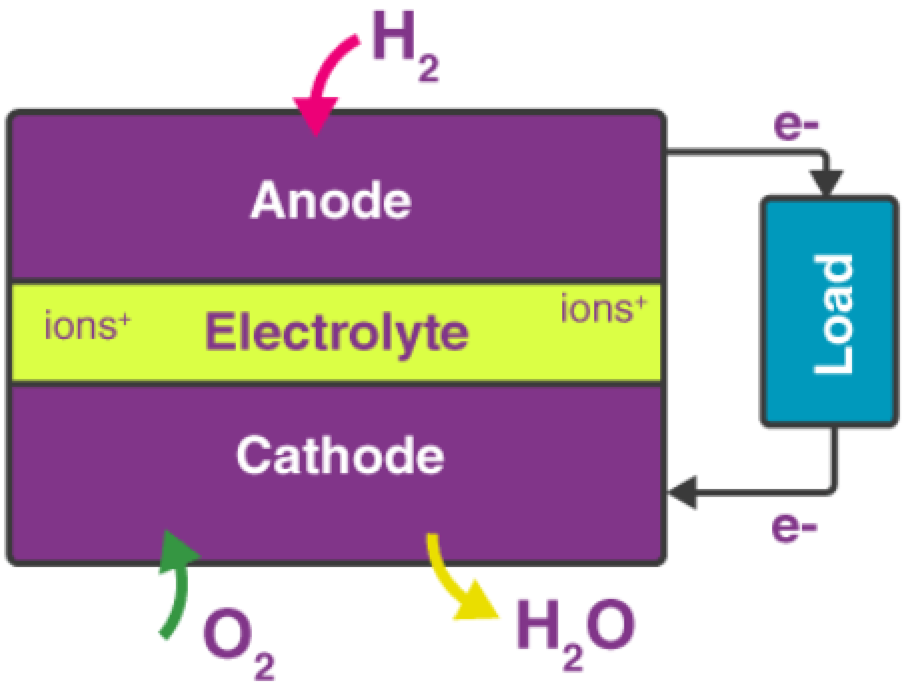
# Working

The reaction between hydrogen and oxygen can be used to generate electricity via a fuel cell.
Such a cell was used in the Apollo space programme and it served two different purposes – It was used as a fuel source as well as a source of drinking water (the water vapour pro duced from the cell, when condensed, was fit for human consumption).

The working of this fuel cell involved the passing of hydrogen and oxygen into a concent rated solution of sodium hydroxide via carbon electrodes. The cell reaction can be writte n as follows:
Cathode Reaction: $\mathbf{O_2 + 2H_2O + 4e^- \rightarrow 4OH^-}$
Anode Reaction: $\mathbf{2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-}$
Net Cell Reaction: $\mathbf{2H_2 + O_2 \rightarrow 2H_2O}$

However, the reaction rate of this electrochemical reaction is quite low. This issue is over come with the help of a catalyst such as platinum or palladium. In order to increase the ef fective surface area, the catalyst is finely divided before being incorporated into the elect rodes.
A block diagram of this fuel cell is provided below.

# Working




The efficiency of the fuel cell described above in the generation of electricity generally approximates to 70% whereas thermal power plants have an efficiency of 40%. This substantial difference in efficiency is because the generation of electric current in a thermal power plant involves the conversion of water into steam, and the usage of this steam to rotate a turbine. Fuel cells, however, offer a platform for the direct conversion of chemical energy into electrical energy.

# Parts of Fuel Cell

- **Anode**
  - Negative post of the fuel cell.
  - Conducts the electrons that are freed from the hydrogen molecules so that they can be used in an external circuit.
  - Etched channels disperse hydrogen gas over the surface of catalyst
- **Cathode**
  - Positive post of the fuel cell
  - Etched channels distribute oxygen to the surface of the catalyst.
  - Conducts electrons back from the external circuit to the catalyst
  - Recombine with the hydrogen ions and oxygen to form water

- **Electrolyte**
  - Proton exchange membrane.
  - Specially treated material, only conducts positively charged ions.
  - Membrane blocks electrons.
- **Catalyst**
  - Special material that facilitates reaction of oxygen and hydrogen
  - Usually platinum powder very thinly coated onto carbon paper or cloth.
  - Rough & porous maximizes surface area exposed to hydrogen or oxygen
  - The platinum-coated side of the catalyst faces the PEM.

# Characteristics of Fuel Cell

- **High energy conversion efficiency**
- **Modular design**
- **Very low chemical and acoustical pollution**
- **Fuel flexibility**
- **Cogeneration (Power & Heat) capability**
- **Rapid load response**

# Types

Despite working similarly, there exist many varieties of fuel cells. Some of these types of fuel cells are discussed in this subsection.

The Polymer /Proton Electrolyte Membrane (PEM) Fuel Cell (Hydrogen Fuel Cell)

Phosphoric Acid Fuel Cell

Solid Acid Fuel Cell

Alkaline Fuel Cell

Solid Oxide Fuel Cell

Molten Carbonate Fuel Cell

# Types

**The Polymer Electrolyte Membrane (PEM) Fuel Cell:**

- These cells are also known as proton exchange membrane fuel cells (or PEMFCs).
- The temperature range that these cells operate in is between $50^oC$ to $100^o$
- The electrolyte used in PEMFCs is a polymer which has the ability to conduct proton s.
- A typical PEM fuel cell consists of bipolar plates, a catalyst, electrodes, and the poly mer membrane.
- Despite having eco-friendly applications in transportation, PEMFCs can also be used for the stationary and portable generation of power.

**Phosphoric Acid Fuel Cell:**

- These fuel cells involve the use of phosphoric acid as an electrolyte in order to chann el the $H^+$
- The working temperatures of these cells lie in the range of $150^oC$ – $200^o$
- Electrons are forced to travel to the cathode via an external circuit because of the non -conductive nature of phosphoric acid.
- Due to the acidic nature of the electrolyte, the components of these cells tend to corro de or oxidize over time.

# Types

**Solid Acid Fuel Cell:**

- A solid acid material is used as the electrolyte in these fuel cells.
- The molecular structures of these solid acids are ordered at low temperatures.
- At higher temperatures, a phase transition can occur which leads to a huge increase in conductivity.
- Examples of solid acids include $CsHSO_4$ and $CsH_2PO_4$ (cesium hydrogen sulfate and cesium dihydrogen phosphate respectively)

**Alkaline Fuel Cell:**

- This was the fuel cell which was used as the primary source of electricity in the Apoll o space program.
- In these cells, an aqueous alkaline solution is used to saturate a porous matrix, which is in turn used to separate the electrodes.
- The operating temperatures of these cells are quite low (approximately $90^oC$).
- These cells are highly efficient. They also produce heat and water along with electrici ty.

# Types

**Solid Oxide Fuel Cell:**

- These cells involve the use of a solid oxide or a ceramic electrolyte (such as yttria-stabilized zirconia).
- These fuel cells are highly efficient and have a relatively low cost (theoretical efficiency can even approach 85%).
- The operating temperatures of these cells are very high (lower limit of 600$^{o}$C, standard operating temperatures lie between 800 and 1000$^{o}$C).
- Solid oxide fuel cells are limited to stationary applications due to their high operating temperatures.

**Molten Carbonate Fuel Cell:**

- The electrolyte used in these cells is lithium potassium carbonate salt. This salt becomes liquid at high temperatures, enabling the movement of carbonate ions.
- Similar to SOFCs, these fuel cells also have a relatively high operating temperature of 650$^{o}$
- The anode and the cathode of this cell are vulnerable to corrosion due to the high operating temperature and the presence of the carbonate electrolyte.
- These cells can be powered by carbon-based fuels such as natural gas and biogas.

# Proton Exchange Membrane Fuel Cell (PEMFC)

## Working Principle of Fuel Cell

- Hydrogen or hydrogen –rich fuel, is fed to the anode where a catalyst separates hydrogen's negatively charged electrons from positively charged ions.
- At a cathode, oxygen combines with electrons and in some cases, with species such as protons or water, resulting in water or hydroxide ions, respectively.
- The electrons from the anode side of the cell cannot pass through the membrane to the positively charged cathode; they must travel around it via an electrical circuit to reach the other side of the cell.
- This movement of electrons is an electrical current.

**At Anode** $2H_2 \rightarrow 4\,H^+ + 4e^-$

**At Cathode** $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

**Overall Reaction** $O_2 + 2H_2 \rightarrow 2H_2O$

# Applications

Fuel cell technology has a wide range of applications.
Currently, heavy research is being conducted in order to manufacture a cost-efficient automobile which is powered by a fuel cell. A few applications of this technology are listed below.

- Fuel cell electric vehicles, or 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 products produced from these cells are heat and 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.
- Fuel cells are also used as primary or backup sources of electricity in many remote areas.

# Case-Study on Industry 4.0

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1. Case-Study Title *

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