# BATTERY TECHNOLOGY

# BATTERY TECHNOLOGY

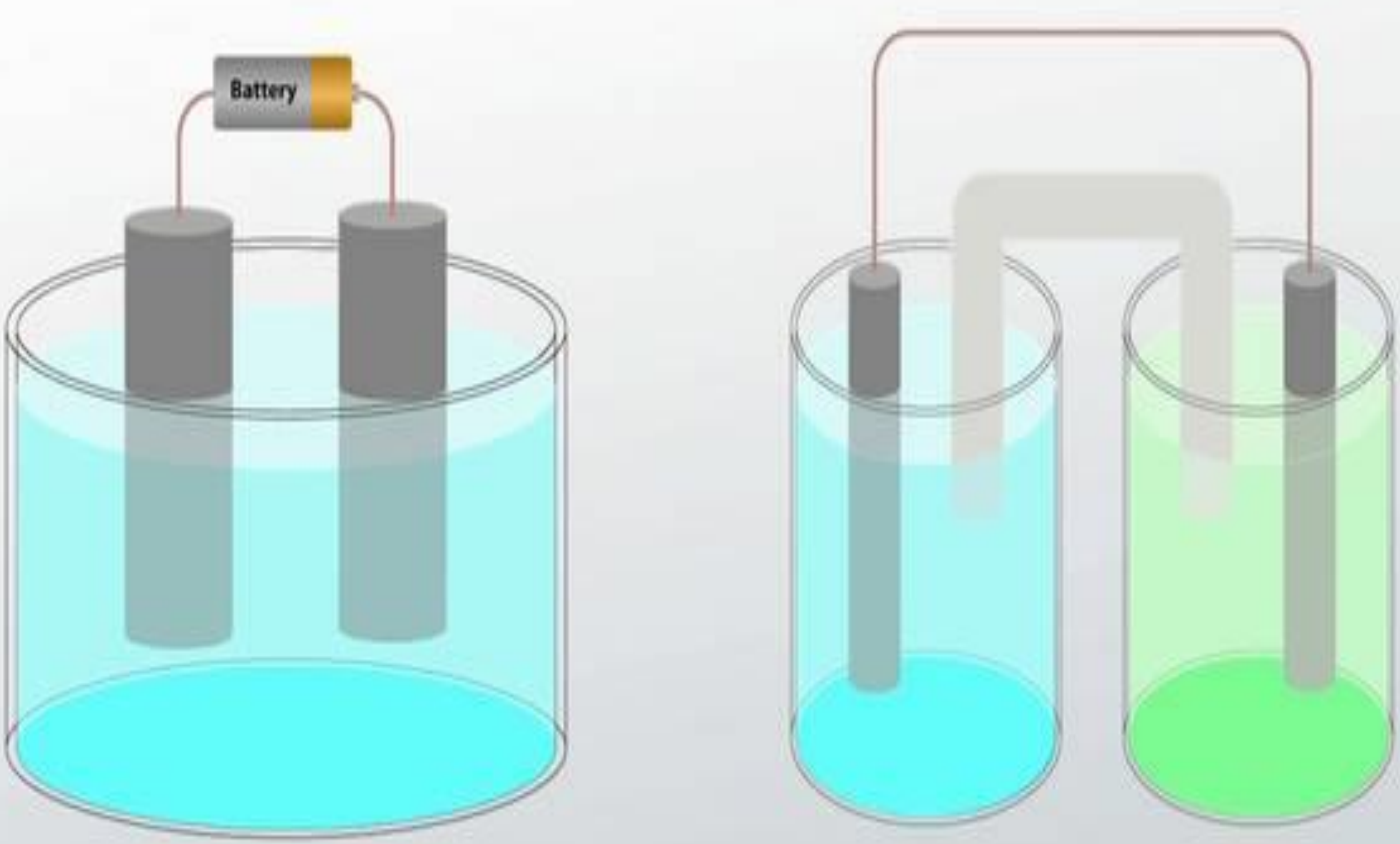
Introduction- definition of cell and battery – Types of cells (reversible and irreversible cells). Battery characteristics: free energy change, electromotive force of battery, power density, energy density- numericals, Memory effect, flat discharge rate.

Primary batteries: Construction and electrochemistry of Zn-C battery, Zn-$Ag_2O$ battery and lithium-$V_2O_5$ battery.

Secondary batteries: Construction and working of lead-acid, Ni-Cd and lithium-ion battery – advantages, limitations and applications.

Fuel cells: Concept, types of fuel cells and merits. Construction, working and applications of methanol-oxygen fuel cell, phosphoric acid fuel cell and Molten carbonate fuel cell.

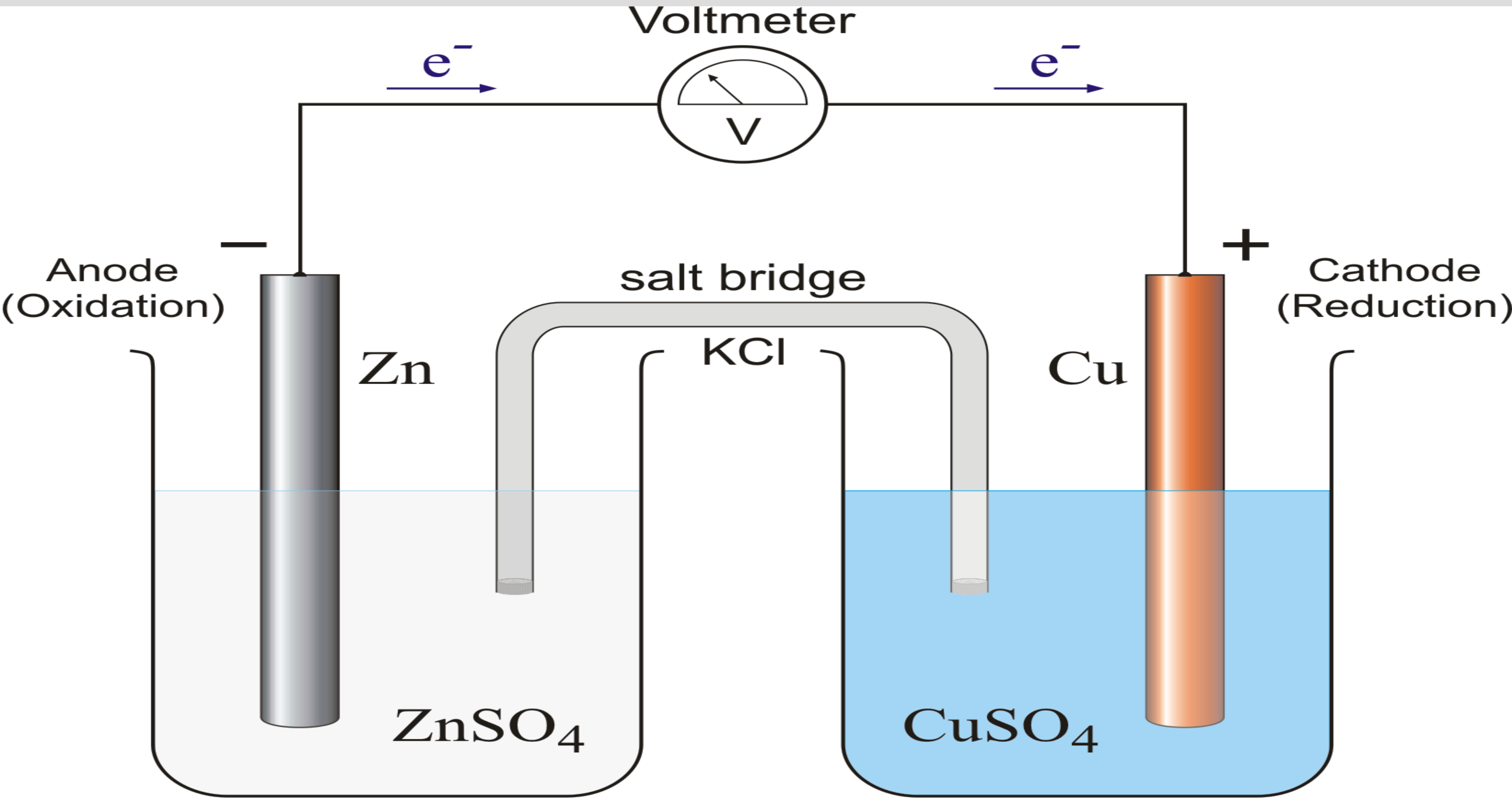
# ELECTROCHEMICAL CELLS




electrolytic

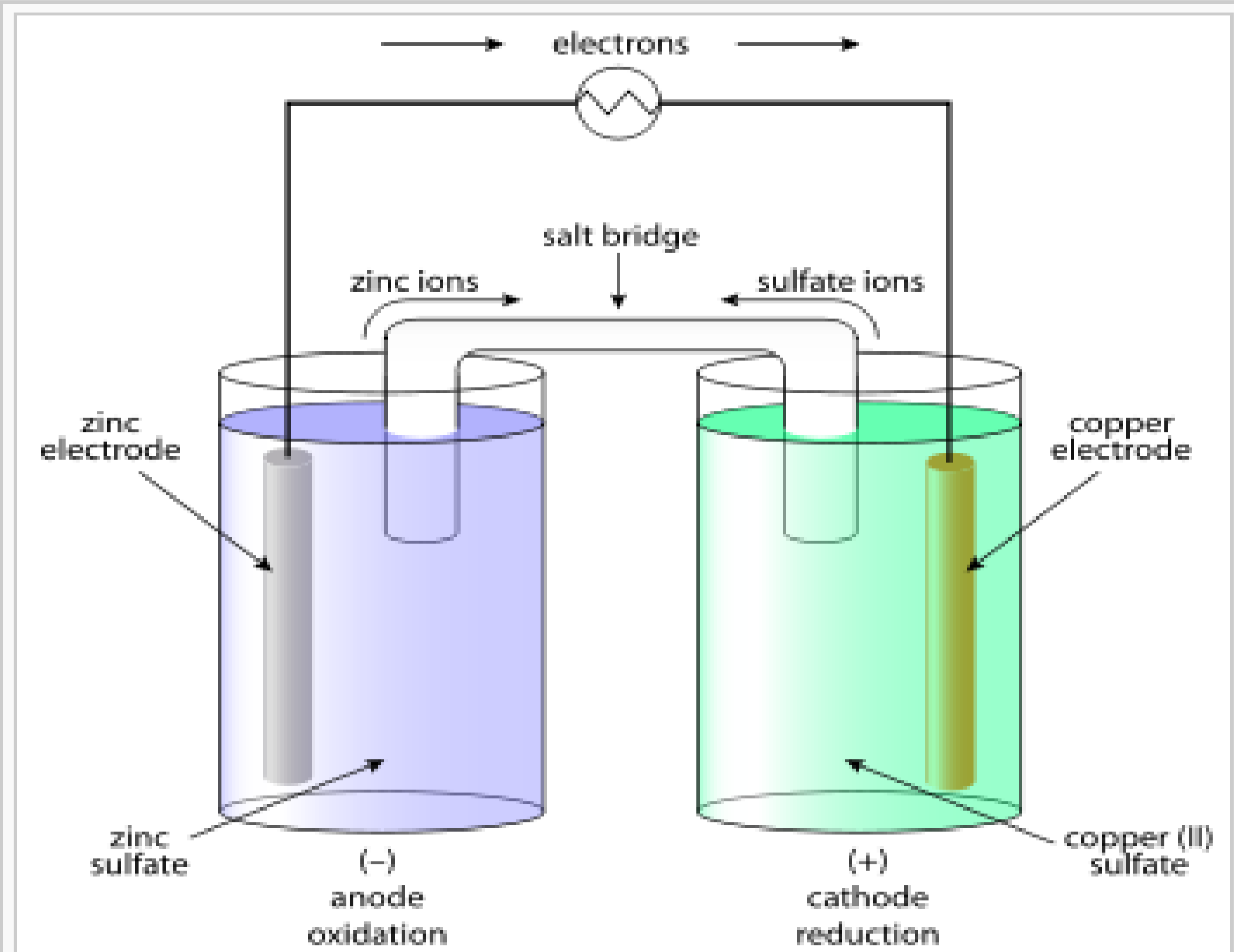
galvanic

# Electrochemical Cell

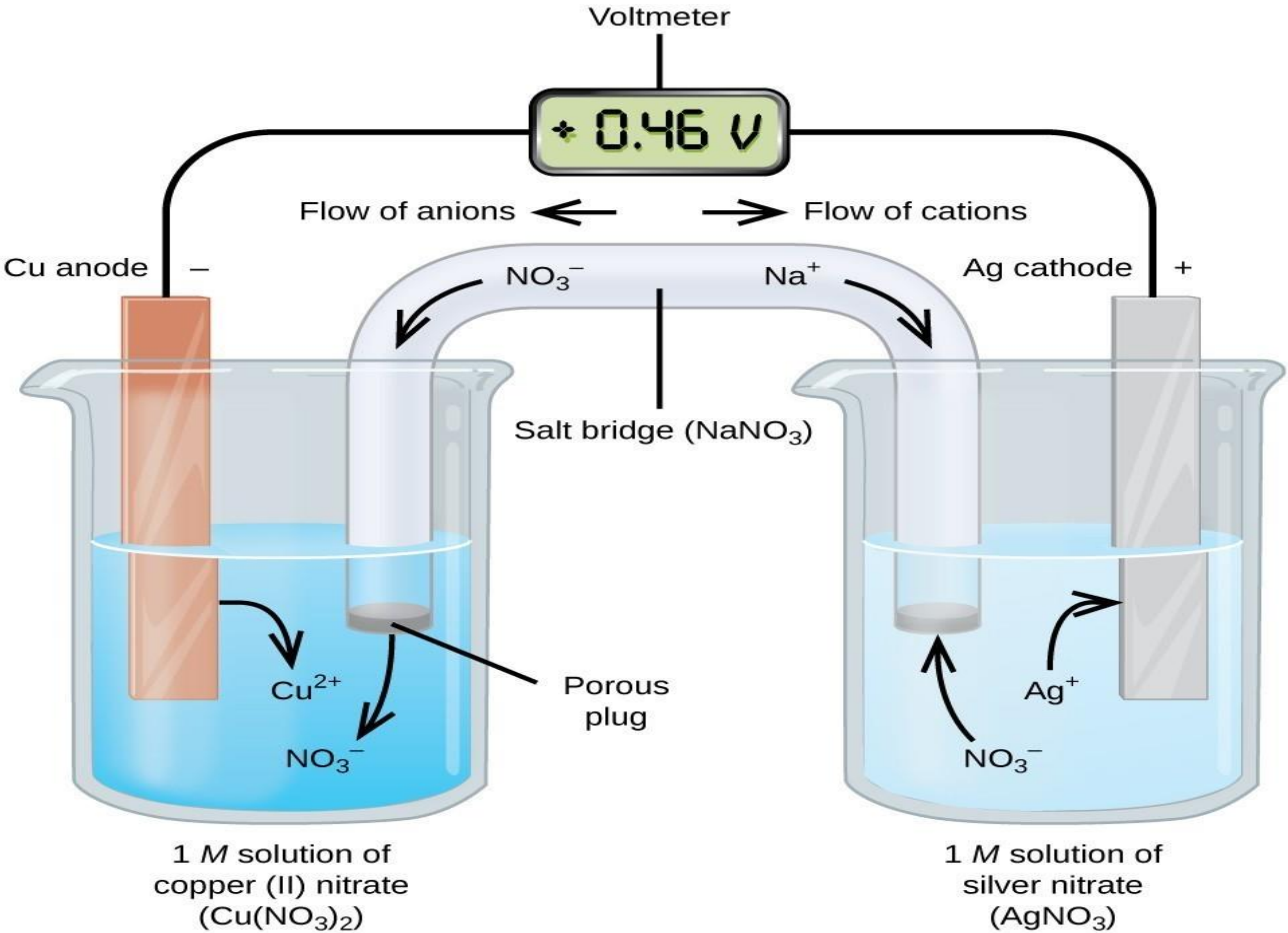



$Zn(s) + 2e^- \longrightarrow Zn^{2+}$ $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

$Zn(s) \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu(s)$



electrons
salt bridge
zinc ions
sulfate ions
zinc electrode
copper electrode
zinc sulfate
copper (II) sulfate
(–)
anode
oxidation
(+)
cathode
reduction



Voltmeter
+0.46 V
Flow of anions
Flow of cations
Cu anode
–
Ag cathode
+
$NO_3^-$
$Na^+$
Salt bridge ($NaNO_3$)
$Cu^{2+}$
$NO_3^-$
Porous plug
$Ag^+$
$NO_3^-$
1 *M* solution of copper (II) nitrate ($Cu(NO_3)_2$)
1 *M* solution of silver nitrate ($AgNO_3$)

Battery is a group of or combination of galvanic cells.

Generally, these cells are connected in series.

Based on the properties, batteries can be classified into 3 types. They are

1. Primary Batteries (P.B)
2. Secondary Batteries (S.B)
3. Fuel cell or Flow batteries.

# Reversible & irreversible cells

**A cell is said to be reversible if the following three conditions are fulfilled**

**(i) The chemical reaction proceeds to produce current from the cell when a smaller external emf than cell emf is applied in opposite direction.**

**(ii) The chemical reaction of the cell stops when an exactly equal external emf is applied.**

**(iii) The chemical reaction of the cell is reversed and the current flows in opposite direction when the external emf is slightly higher than that of the cell.**

**Example: Daniell cell ($Cu^{2+} + Zn \leftrightarrow Cu + Zn^{2+}$)**

Any cell which does not obey all three conditions is an irreversible cell. Example: Dry cell or any primary cell.

| Reversible Cells | Irreversible Cells |
|---|---|
| A cell which obeys the three conditions of thermodynamic reversibility is called reversible cell. | Cells which do not obey the conditions of thermodynamic reversibility are called irreversible cells. |
| Cell reaction is reversed when external potential greater than cell potential is applied. | The cell reaction is not completely reversed. |
| Daniel cell, secondary batteries. (allrechargeable/secondary batteries). | Zinc – silver oxide cell, Dry cell.(Primary Cells) |

## Differences between Primary & Secondary Battery

| Primary Battery | Secondary Battery |
|---|---|
| 1.cell reaction cannot be reversed | 1. cell reaction can be reversed |
| 2.cell cannot be recharged | 2.cell can be recharged |
| 3.There is a limited life period | 3.cell can be used again and again |
| 4.It is not a storage battery<br>Ex:-1. Dry cell (Leclanche cell)<br>2.Zn-C battery<br>3.Lithium battery | 4.it is a storage battery<br>Ex:-1. Lead -acid battery<br>2.Ni-cd battery<br>3.Li-ion battery |

# Primary & secondary batteries

**In other words, the net cell reactions of battery can be reversed. Secondary batteries consists of reversible cells. Hence, the electrochemistry is reversible, and they can be rechargeable. They are known as storage batteries, Since they store electrical energy. Example: Lead–acid battery and Ni–Cd battery.**

**The secondary batteries have advantages over the other primary batteries that the net cell reactions can be reversed during the charging process and the current can be drawn during the discharge process. A secondary battery works as galvanic cell while discharging and works as electrolytic cell during charging.**

# Battery characteristics:

**Free energy change,**

**Electromotive force of battery,**

**Power density**

**Energy density- numericals**

**Memory effect, &**

**flat discharge rate.**

# Free energy change

**Whenever spontaneous redox reaction occur in a battery, there is a decrease in free energy of the system.**

$$-\Delta G = nFE$$

**where F = Faraday (~ 96500 C)**

**n = number of electrons involved in electrode reactions.**

**E = potential generated in Volts.**

**The magnitude of free energy change in the overall cell reaction directly proportional to the voltage of a battery and hence on the choice of electrode systems.**

# Electromotive force of battery (EMF)

$$E_B = E^o_{cell} - \frac{2.303RT}{nF} \log_{10}\left[\frac{M_1^{n+}}{M_2^{n+}}\right]$$

**It is evident, therefore, that the EMF of the cell of a battery is dependent on.**

**(i) Potential difference between the cathode and anode,**

**(ii) The ratio of the ionic concentration of $M_1^{n+}$ and $M_2^{n+}$, and**

**(iii) The temperature.**

**It can be remarked that**

**EMF of the battery is higher, if the electrode potential difference between the two electrodes is more.**

**EMF of the cell decreases with the increasing molar concentration of $[M_1^{n+}]$ in the numerator of the expression.**

**If the temperature of the battery increases, the EMF of the cell gets reduced marginally.**

# Electromotive force of battery (EMF)

**It is not always possible to construct a suitable galvanic cell of desired EMF and capacity. In such case, the desired EMF, current can be achieved by connecting the cells in series or parallel or as series and parallel arrays.**

**An automotive battery is a rechargeable battery that is used to start a motor vehicle. For a car it requires ~ 12 V battery.**

**Depending on battery chemistry**

| | | |
|---|---|---|
| Nickel Cadmium | 1.2 | volts +/- |
| Nickel Metal Hydride | 1.2 | volts +/- |
| Lead Acid Cells | 2 | Volts +/- |

**To create this voltage, six number of cells of lead acid are connected in series. It also can prepare a battery from 10 NiMH cells.**

# Power density

**The power density is usually discussed in terms of the cell mass:**

**Power density = Power/mass (units are W/kg)**

**= Energy (E)/time (t)/mass (kg)**

**= Energy (q X V)/time (t)/mass (kg) of cell**

**The ratio of the power delivered by a cell or a battery to its weight, W/kg, is also known as the power density of a battery.**

**During the discharge of a battery, the power density decreases.**

**This is related to the energy density at a given discharge rate and indicates how rapidly the cell can be DISCHARGED and how much power generated. A cell with high energy density may exhibit a significant voltage and capacity drop at higher discharge rates and power density, therefore, has a low power density.**

# Energy density

**The energy density or capacity is determined by the voltage of the cell and the amount of charge that can be stored,**

$$E = q \times V$$

**This parameter is usually evaluated on a weight or volume basis:**

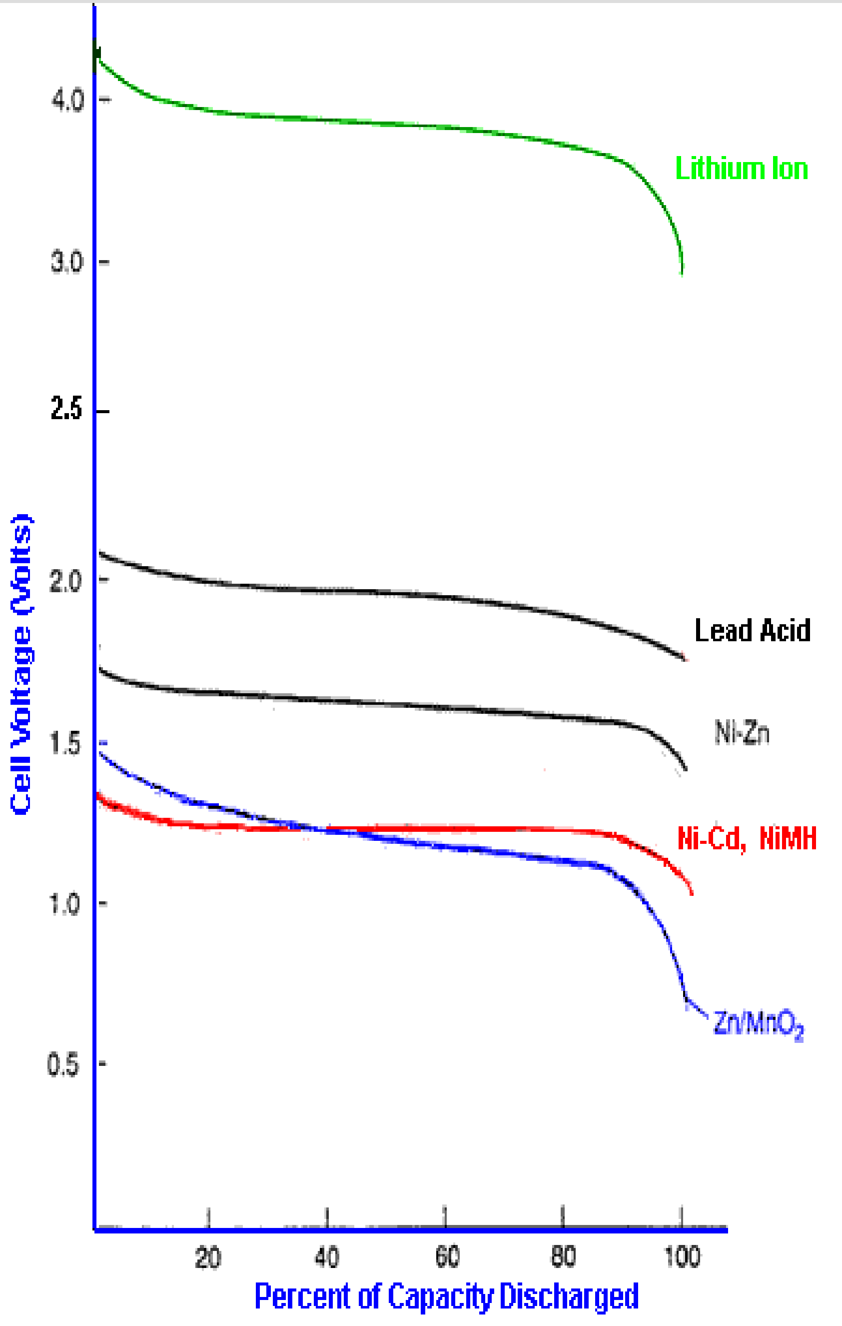
**Theoretical. weight. capacity = q x V/mass (units are W h/kg)**

**Theoretical. volume. capacity = q x V/volume (units are Watt h/L)**

**The energy density of a cell or a battery is also described as the ratio of the energy output of a cell or battery to its weight, Wh/kg**

# flat discharge rate

- The discharge curve is a plot of voltage against percentage of capacity discharged.
- A flat discharge curve is desirable as this means that the voltage remains constant as the battery is used up.
- Typical voltage range from 1.2 V for a Ni/Cd battery to **3.7 V for a Li/ion battery**.

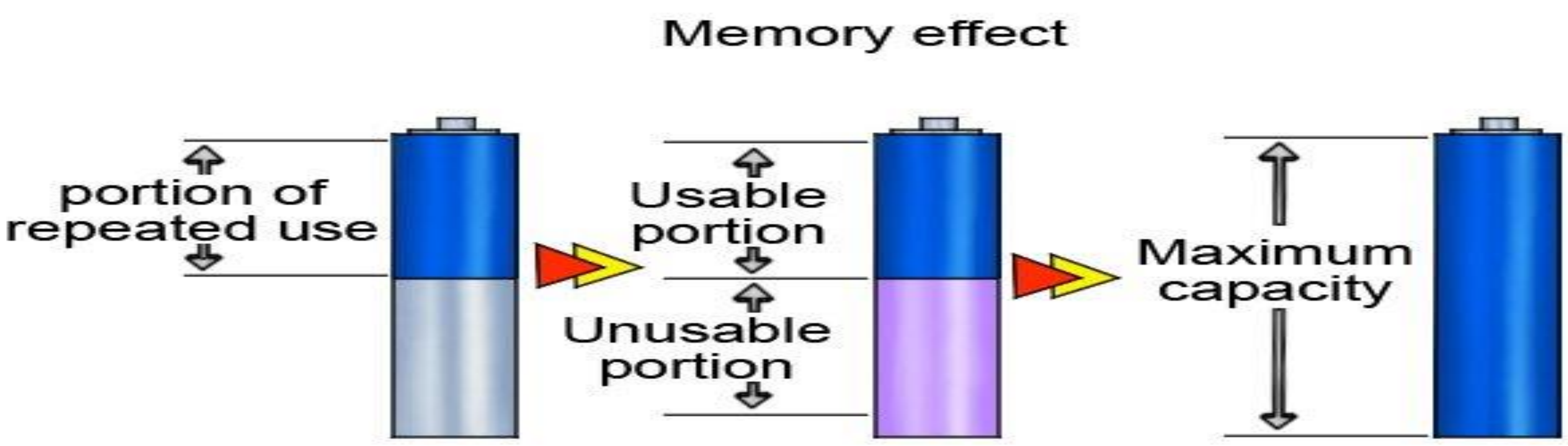


# Memory effect

Memory effect is observed in rechargeable batteries, that causes them to store less power. The other terms used for memory effect are **battery effect, lazy battery effect or battery memory.**

This effect occurs when during discharge, the battery does not discharge fully every time, resulting in residual charge. After repeated charging, that residual charge increases to a point where battery can store only a small amount of useful charge.

Memory effect observed in NiCd , Li-Ion and NiMH batteries.



# Primary (Disposable) Batteries Applications

- Zinc carbon (flashlights, toys)
- Heavy duty zinc chloride (radios, recorders)
- Alkaline (all the above)
- Lithium (photoflash)
- Silver, mercury oxide (hearing aid, watches)

# Zinc - Carbon Battery

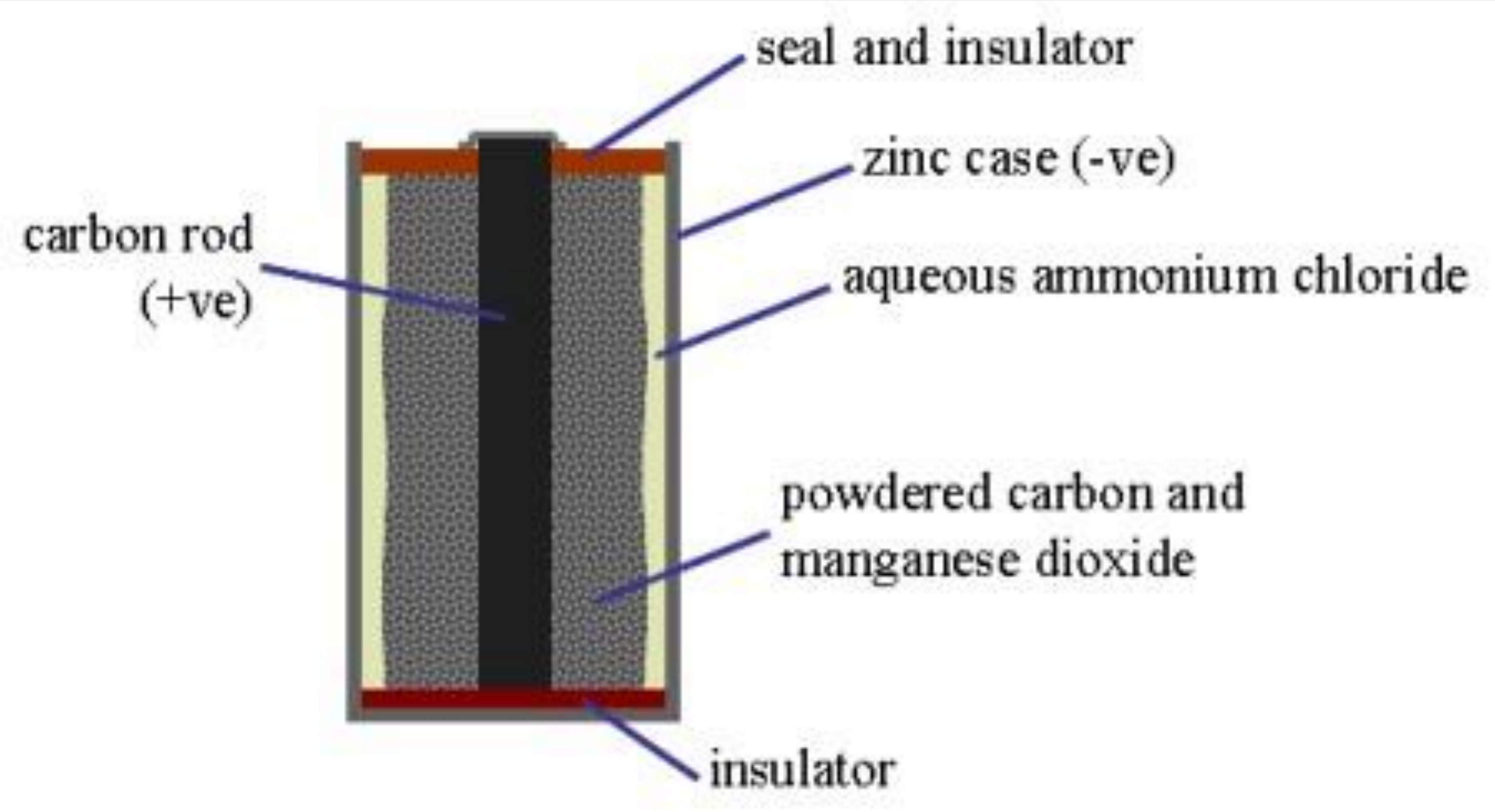
- Chemistry

  Zinc (-), manganese dioxide (+)

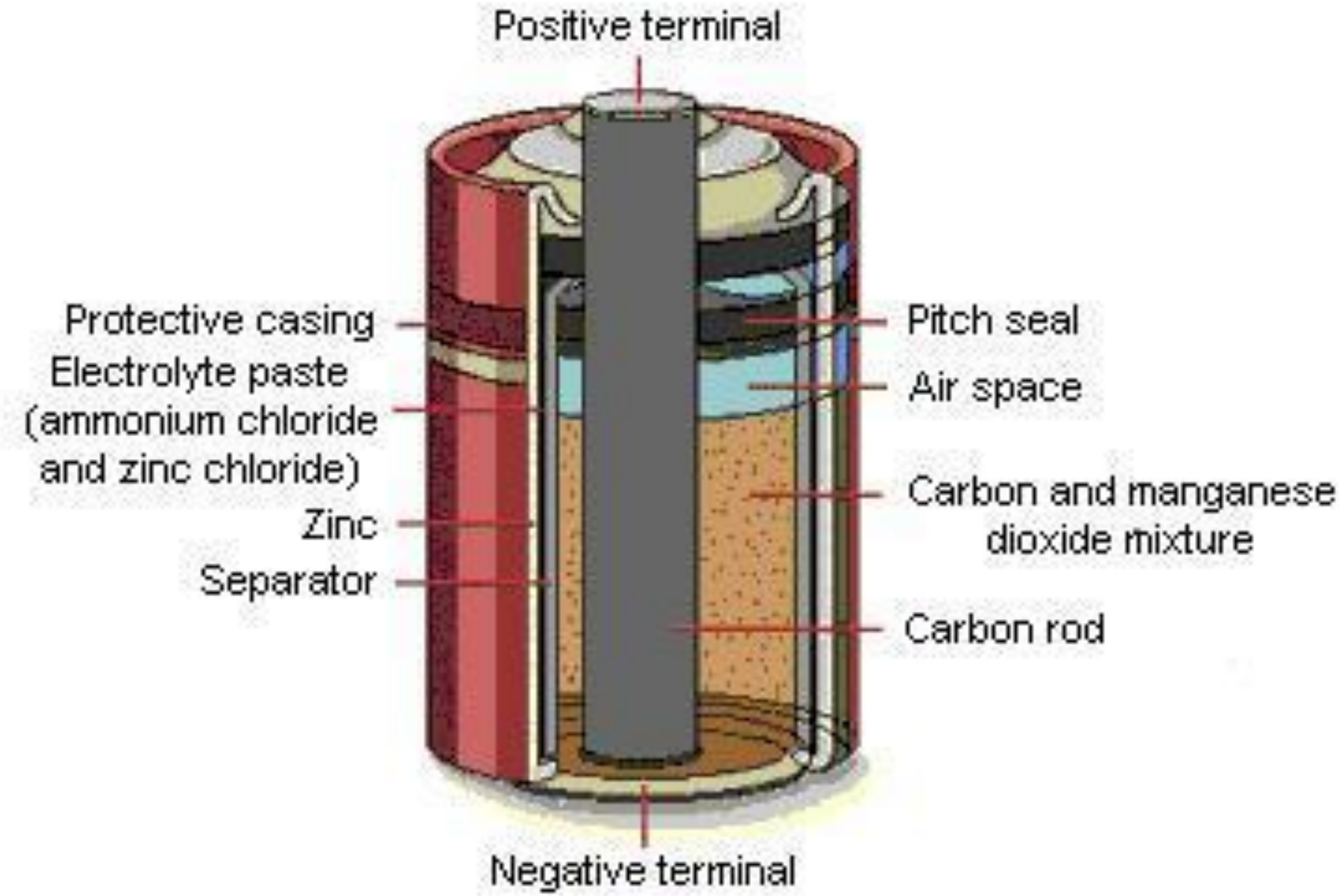
  Aqueous ammonium chloride electrolyte

- Features
  - + Inexpensive, widely available
  - Inefficient at high current drain
  - Poor discharge curve
  - Poor performance at low  and high temperatures

# Zinc - carbon or Leclanche Cell or Dry Cell




**Cell notation:** $Zn/Zn^{+2}//NH^{+}_{4}/MnO_{2}, C$




**Leclanche Cell (or) Dry Cell :**

# Reactions:

**At anode:**

$$Zn \longrightarrow Zn^{+2} + 2e^-$$

**At cathode:**

$$MnO_2 + 2e^- + 2H_2O \longrightarrow 2MnO(OH) + 2OH^-$$

**Side reactions:**

$$2OH^{--} + 2NH_4Cl \longrightarrow 2NH_3 + 2H_2O + 2Cl^-$$

$$Zn^{+2} + 2NH_3 + 2Cl^- \longrightarrow [Zn\,(NH_3)_2Cl_2]$$

**Total reaction:**

$$Zn + MnO_2 + NH_4Cl \longrightarrow [Zn\,(NH_3)_2Cl_2] + 2H_2O$$

# Primary Alkaline Battery

- Chemistry :

  Zinc (-), manganese dioxide (+)

  Potassium hydroxide aqueous electrolyte

- Features :

  50-100% more energy than carbon zinc

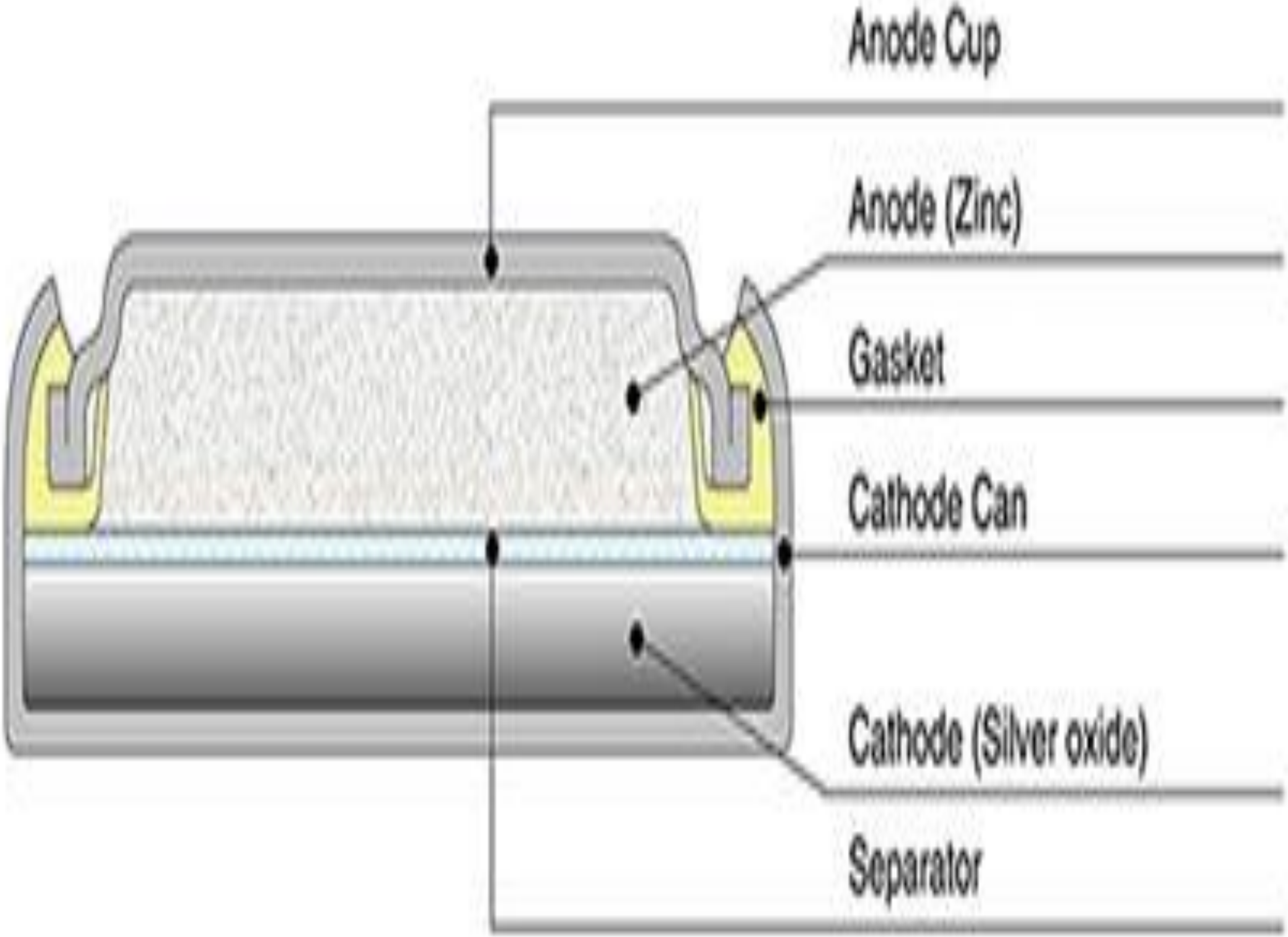
  Low self-discharge

  long-life

  Poor discharge curve

# Zn-$Ag_2O$ battery: Alkaline Primary Battery

- It is in the sold in the market as button type
- In this $Ag_2O$ is pressed into the thin button type metal case which act as cathode .
- absorbent material soaked in KOH is placed in between the anodic and cathodic compartments.
- zinc metal is at the centre of the cell which act as the anode of the cell.
- KOH acts as electrolyte.


Anode Cup
Anode (Zinc)
Gasket
Cathode Can
Cathode (Silver oxide)
Separator

- **At anode:**

$$Zn + 2\,OH^- \longrightarrow ZnO_{(S)} + H_2O + 2e^-$$

- **At cathode:**

$$Ag_2O_{\,(S)} + H_2O + 2e^- \longrightarrow 2\,Ag_{(S)} + 2\,OH^-$$

- **Overall cell reaction:**

$$Zn + Ag_2O_{\,(S)} \longrightarrow ZnO_{(S)} + 2\,Ag_{(S)} + E.E.$$

| | |
|---|---|
| Anode Reaction | $Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$ |
| Cathode Reaction | $Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^-$ |
| Total Battery Reaction | $Ag_2O + Zn \rightarrow 2Ag + ZnO$ + E.E. |

voltage of this cell is 1.5V.

it has high capacity and potential remains constant till its shelf life.

this cell offers better cell performance than others because of its high voltage ,longer life more reliability and nontoxic.

The cells used extensively in electronic watches, calculators and small electronic gadgets etc.

# Lithium –vanadium pentoxide ($Li/V_2O_5$ ) battery

- It is a primary battery and **reserve type** battery
- Anode: lithium
- Cathode: 90% V2O5 & 10% graphite (weight basis)
- Electrolyte: 2M LiAsF6 + 0.4 M LiBF4 in methylformate
- Separator: micro porous polypropylene
- Cell voltage is **3.2 V**, has high volumetric energy density
- Mainly used as a **RESERVE BATTERY.**

## At anode:

$$Li \longrightarrow Li^{+} + e^{-}$$

## At cathode:

$$V_2O_5 + Li^{+} + e^{-} \longrightarrow Li\,V^{+5}_{2-X}\,V^{+4}_{X}\,O_5$$

## Overall cell reaction:

$$V_2O_5 + Li \longrightarrow Li\,V^{+5}_{2-X}\,V^{+4}_{X}\,O_5 + EE.$$

# Secondary (Rechargeable) Batteries

- **Lead acid (acidic)**
- **Nickel - Cadmium (alkaline)**
- **Lithium - ion**

# Lead Acid Batteries

- **Chemistry**

  Anode-Lead(-),

  Cathode-lead di oxide(+)

  Electrolyte -Sulfuric acid (sp gr-1.2)

- **Features**

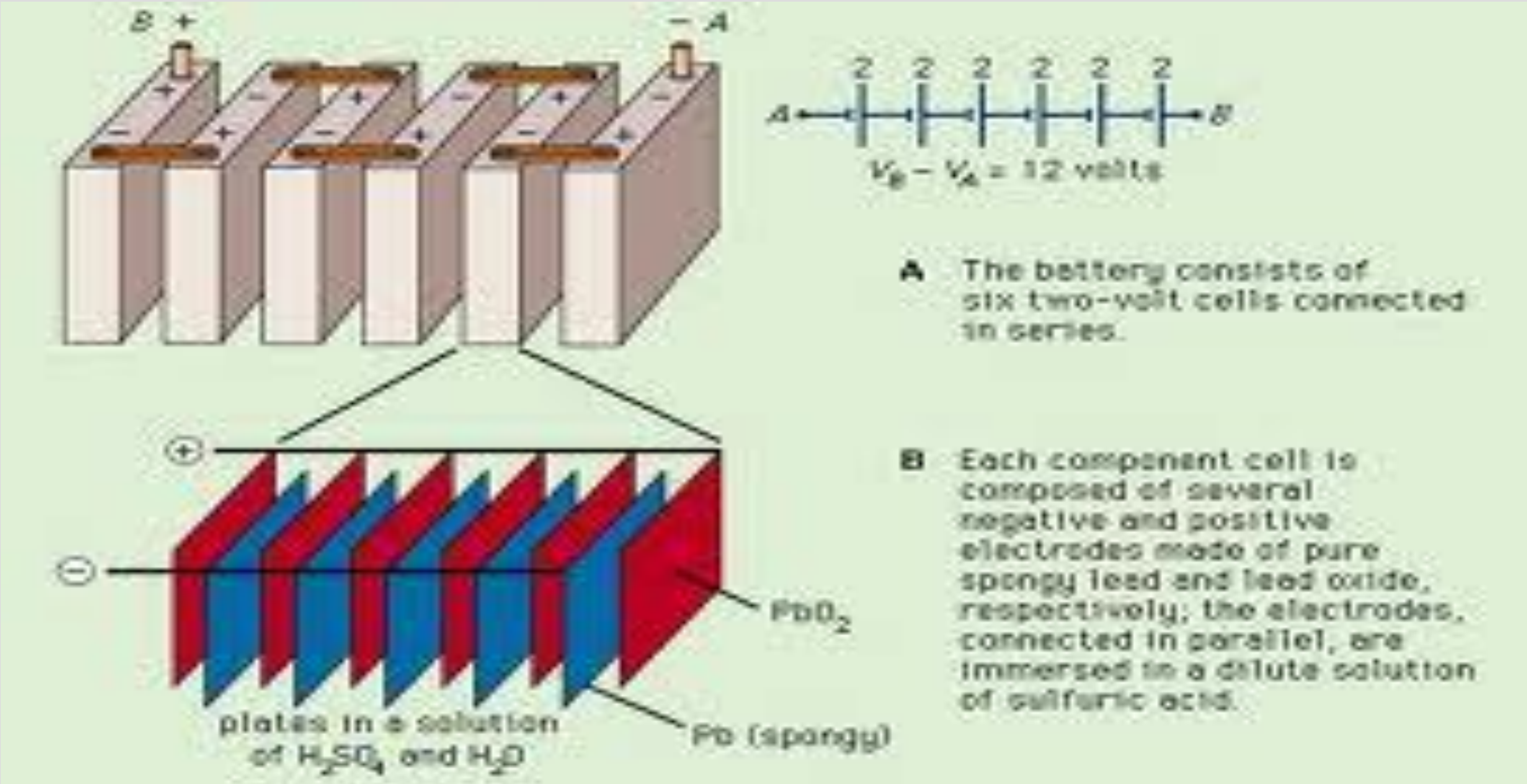
  Least expensive

  Durable

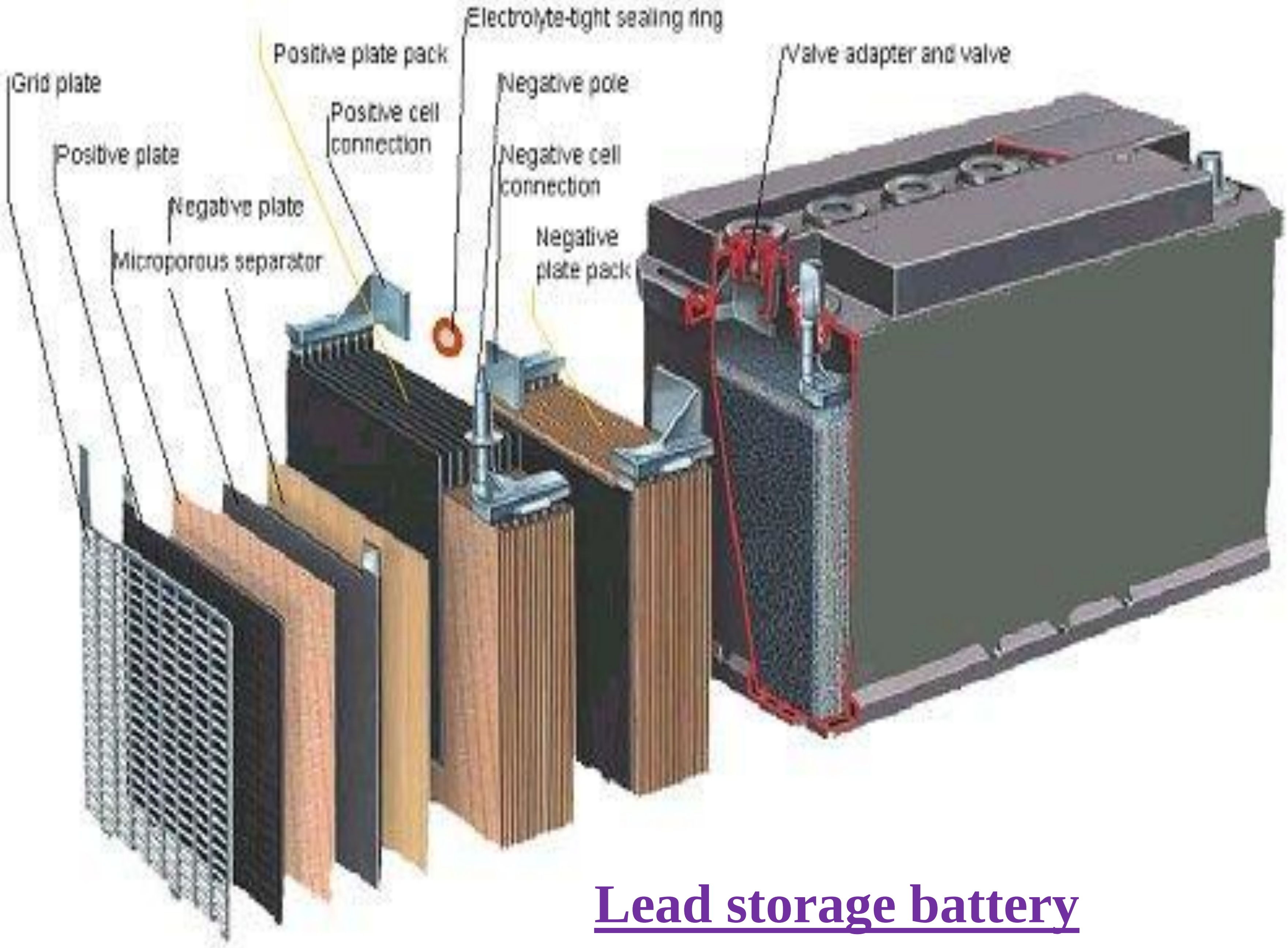
  Low energy density

  Toxic

# Lead acid battery




**$Pb, PbSO_4$ // $H_2SO_4$ / $PbSO_4$, $PbO_2$ / $Pb$**




**Lead storage battery**

## During discharging

### At anode:

$$Pb \longrightarrow Pb^{+2} + 2e^-$$

$$Pb^{+2} + SO^{-2}_4 \longrightarrow PbSO_4$$

### At cathode:

$$PbO_2 + 2e^- + 4H^+ \longrightarrow Pb^{+2} + 2H_2O$$

$$Pb^{+2} + SO^{-2}_4 \longrightarrow PbSO_4$$

### Net reaction:

$$Pb + PbO_2 + 4H^+ + 2SO^{-2}_4 \longrightarrow 2\,PbSO_4 + 2H_2O + E.E$$

## During charging:

### At anode:

$$PbSO_4 + 2e^- \longrightarrow Pb + SO^{-2}_4$$

### At cathode:

$$PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO^{-2}_4$$

### Net reaction:

$$2\ PbSO_4 + 2H_2O + E.E \longrightarrow Pb + PbO_2 + 4H^+ + 2SO^{-2}_4$$

**for charging cell is connected to external source having higher voltage.**

# Lead Acid

- Low self-discharge
- 40% in one year (three months for NiCd)
- No memory
- Cannot be stored when discharged
- Limited number of full discharges
- Danger of overheating during charging

# Nickel Cadmium Batteries

- **Chemistry**

  Cadmium (-), nickel oxyhydroxide (+)

  Potassium hydroxide aqueous electrolyte

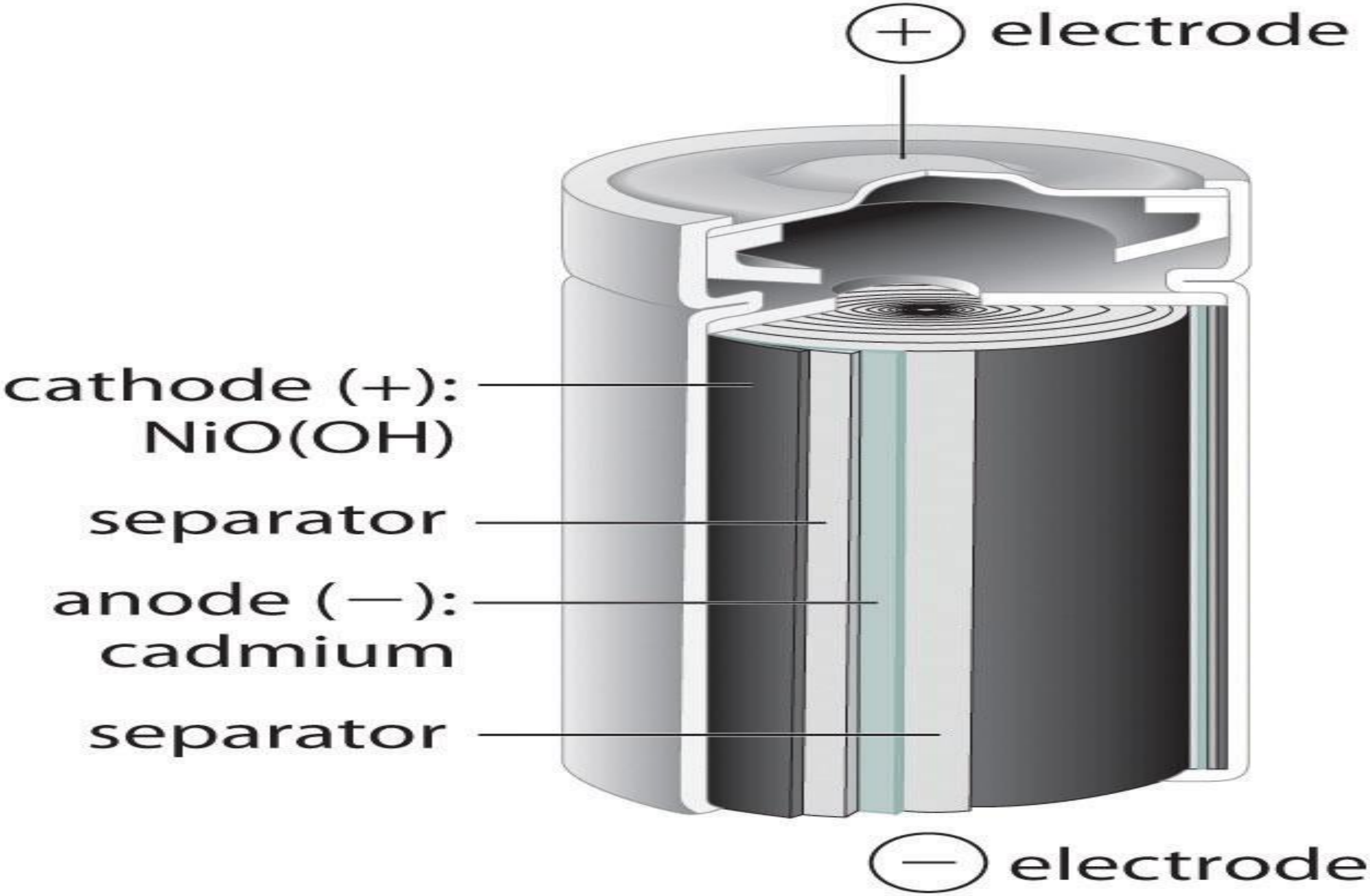
- **Features**

  long life, economical

  Good high discharge rate

  Relatively low energy density

  Toxic




cell reaction:

$$Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \longrightarrow$$
$$Cd(OH)_2(s) + 2Ni(OH)_2(s)$$

**At anode:**

$$Cd \longrightarrow Cd^{+2} + 2e^-$$

$$Cd^{+2} + 2OH^- \longrightarrow Cd(OH)_2$$

**At cathode:**

$$2NiO(OH) + 2e^- + 2H_2O \longrightarrow Ni(OH)_2 + 2OH^-$$

# Ni-Cd Recharging

- Over 1000 cycles (if properly maintained)
- Fast, simple charge
- Self discharge

  10% in first day, then 10% in month
- Memory effect

  Overcome by 60% discharges to 1.1V

# Secondary Alkaline Batteries

- **Features**
  - 50 cycles at 50% discharge
  - No memory effect
  - Shallow discharge better than deeper

# Lithium Ion Batteries

- Chemistry

  Graphite (-), cobalt or manganese (+)

  Nonaqueous electrolyte

- Features

  40% more capacity than NiCd

  Flat discharge

  Self-discharge 50% less than NiCd

  Expensive

# Lithium Cobalt Oxide($LiCoO_2$) example of Li-ion battery

Its high specific energy make Li-cobalt the popular choice for cell phones, laptops and digital cameras.

The battery consists of a cobalt oxide cathode and a graphite carbon anode.

The cathode has a layered structure and during discharge lithium ions move from the anode to the cathode. The flow reverses on charge.

The drawback of Li-cobalt is a relatively short life span and limited load capabilities (specific power).

Anode: $Li_xC$ (graphite intercalated Lithium compound)

Cathode: $LiMO_2$ (Transition metal intercalated lithium compound like $LiCoO_2$

Electrolyte: LiX (Lithium salts like $LiClO_4$)

Solvent: non aqueous solvents like Propylene carbonate (PC) – Ethylene Carbonate (EC)

Binder: Poly vinylidene fluoride

**Insulator/separator:** poly propylene

**Anode & Cathode current collectors:** Copper and Aluminum foils

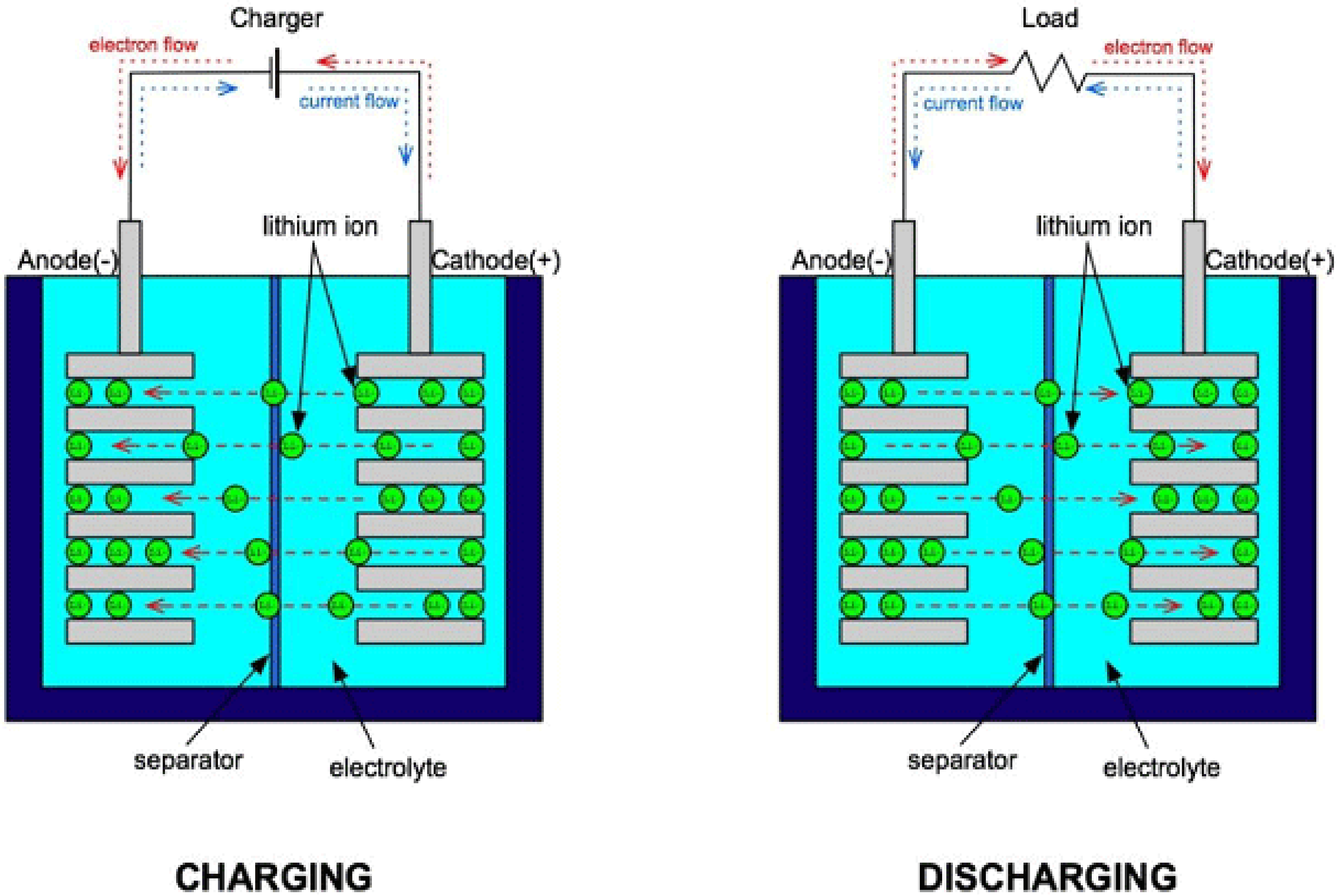
**$Li_x C$ / LiX in PC-EC / $Li_{(1+x)} MO_2$ (cell notation)**

## During the discharge following reactions take place

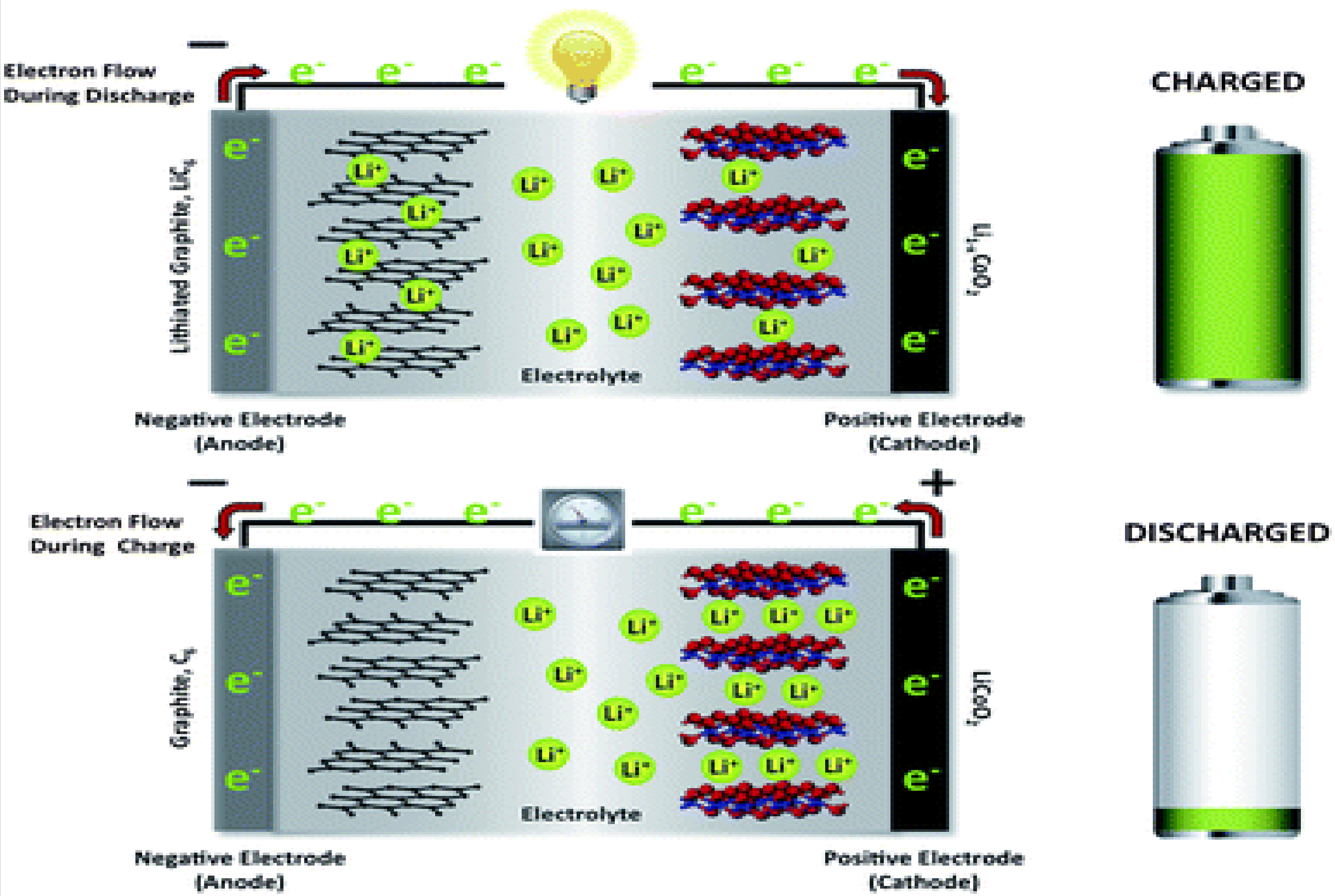
$$Li_xC \longrightarrow C + X\,Li^+ + Xe^-$$

$$LiMO_2 + XLi^+ + Xe^- \rightarrow [Li]_{1+x}\,MO_2$$

$$Li_xC + LiMO_2 \longrightarrow Li_{(x+1)}\,MO_2 + C + EE$$


Charger
electron flow
current flow
lithium ion
Anode(-)
Cathode(+)
separator
electrolyte
CHARGING
Load
electron flow
current flow
lithium ion
Anode(-)
Cathode(+)
separator
electrolyte
DISCHARGING

# How Lithium-Ion Batteries Work



# Lithium Ion Recharging

- 300 cycles
- 50% capacity at 500 cycles

## Fuel cells:

Concept, types of fuel cells and merits.

Construction, working and applications of

methanol-oxygen ,

phosphoric acid fuel cell, and

Molten carbonate fuel cell.

# Fuel cell

- In these cells fuel and oxidant should be supplies continuously in order to get current.
- It is highly eco friendly i.e. there is no harmful products.
- fuel cell technology is playing an important role in modern technology.

# classification

Based on working temperature they are 3 types.

1.Low temperature fuel cells

2. Moderate temperature fuel cells

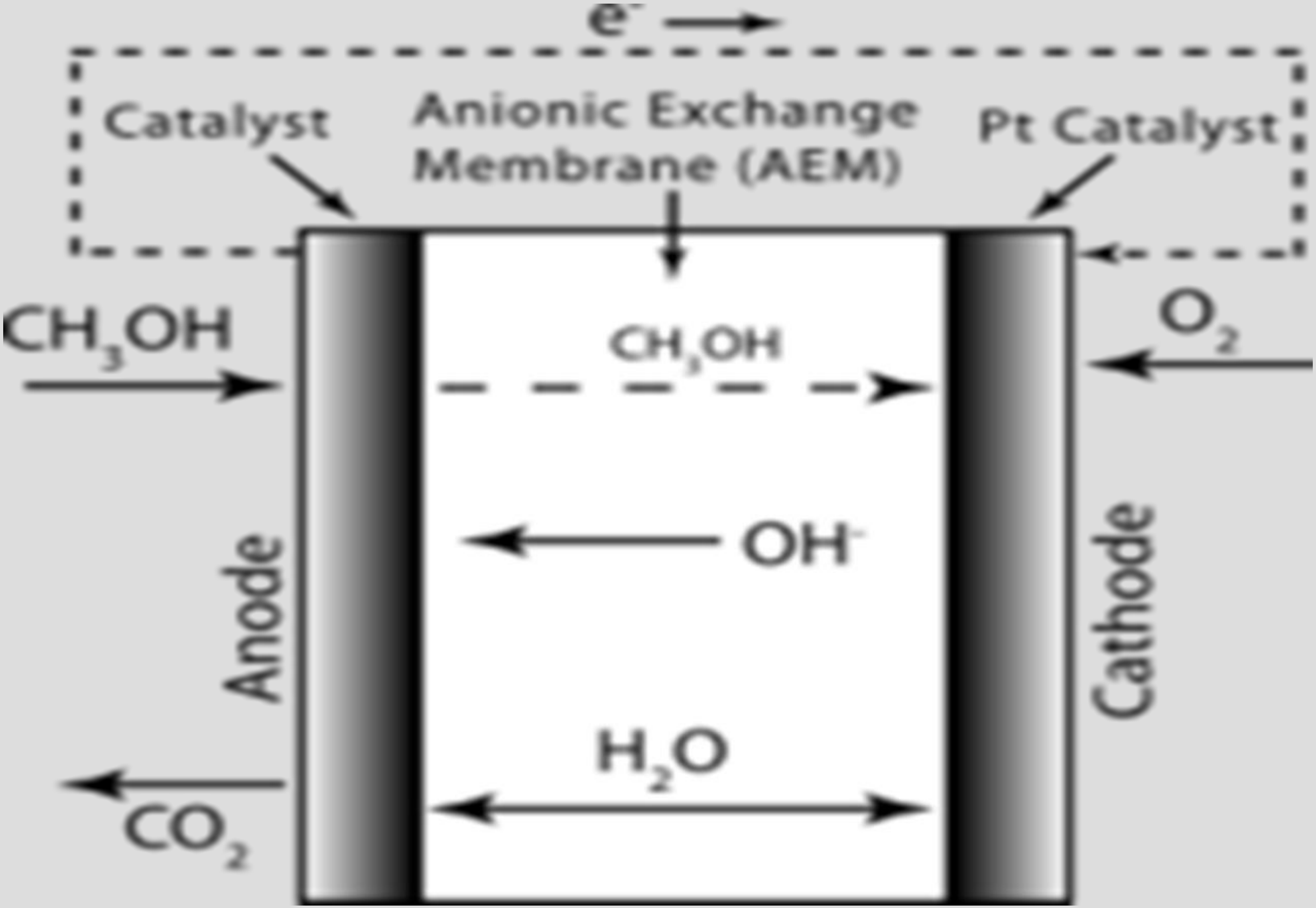
3. High temperature fuel cells

## Based on electrolytes

They are 6 types.

1. Alkaline fuel cells
2. Phosphoric acid (acidic) fuel cells
3. Molten carbonate fuel cells
4. Solid oxide fuel cells
5. Biochemical fuel cells
6. Polymer electrolyte membrane fuel cells.

# Methanol-Oxygen Alkaline fuel cells



| | |
|---|---|
| Fuel | : Methanol |
| Oxidant | : Oxygen |
| Electrolyte | : KOH |
| Electrolyte state | : Liquid |

Electrodes: (i) Anode: Porous Ni impregnated with Pt/ Pd catalyst

(ii) Cathode: Porous Ni coated with silver catalyst

| | |
|---|---|
| Catalysts | : Pt/ Pd & Ag |
| Charge carrier | : $(OH^-)$ ions |
| Operating temp | : 40-90$^o$ C |
| Co-generating heat | : Low quality |
| Fuel cell efficiency | : 40-45% power |

## At anode:

$$CH_3OH + 6OH^- \longrightarrow CO_2 + 5H_2O + 6e^-$$

## At cathode:

$$3/2O_2 + 6e^- + 3H_2O \longrightarrow 6OH^-$$

## Net reaction:

$$CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + 2H_2O + E.E.$$

Reference books

# **Engineering chemistry**

- PC Jain & M Jain
- Sashi Chawla
- OG Palanna