

## Unit 1

### Battery Technology

- **Battery Technology**

**Introduction to batteries: Redox reactions and electron transfer, the basic principles behind battery operation. Electrochemical cells: anode, cathode, electrolyte, and their roles in energy conversion. Key battery performance metrics. Emerging Battery Technologies, Lead-acid batteries (working principles and applications), Nickel-metal hydride batteries (improved efficiency, environmental advantages, and limitations), Lithium-ion batteries (chemistry variations and performance characteristics), exploring alternative chemistries (sodium-ion, solid-state, and organic batteries). Limitations and Sustainability Concerns: Charge and discharge cycles: battery degradation, Safety concerns with lithium-ion batteries: thermal runaway, fire hazards, Environmental impact of battery production (resource extraction, mining, and pollution).**

### INTRODUCTION

Can you imagine a world without batteries? The clock on your wall requires a battery for it to work. The watch on your wrist goes on a battery. The motor vehicle needs a battery for it to start and take you to your destination. Battery is the backbone of UPS to run your computer without interruption. After a day's work, if you pick-up the remote control of the television, it is again the battery that helps you to change channels of the T.V. Cameras, laptop computers, cellular phones, key chain laser, heart pacemaker and children's toys – they all require batteries.

Batteries are used for so many different purposes and different applications require batteries with different properties. The battery required to start a car must be capable of delivering a large electrical current for a short period of time. The battery that powers a cardiac pacemaker must be small, rugged, leak proof, compact and capable of delivering a steady current for an extended period of time. In UPS systems, longer and consistent backup is needed. Batteries for hearing aids must be above all tiny. Batteries for torpedoes and submarines must be stable during storage and give high power for short times & certainly rechargeable. For a lap-top computer, a battery in the form of a flexible sheet distributed around the case is much preferred. Batteries remain an enormous industry with a turnover of billions of pounds worldwide.

**Primary batteries:** They are galvanic cells which produce electricity from chemicals that are sealed into it when it is made. This type of cells cannot be recharged as the cell reaction cannot be reversed efficiently by recharging. Once the cell reaction has reached equilibrium the cell must be discarded. No more electricity is generated, and we say the battery is 'dead'. These are also known as 'throw – away' batteries or irreversible batteries. Eg: Dry cell, Lithium copper sulfide cell.

**Secondary batteries:** A secondary cell is rechargeable by passing current through it. In the charging process, an external source of electricity reverses the spontaneous cell reaction and restores a non- equilibrium mixture of reactants. After charging, the cell can be used for supplying current when required, as the reaction sinks toward equilibrium again. Thus, as the secondary cell can be used through a large number of cycles of discharging and charging. Such cells are also known as rechargeable cells, storage cells, or accumulators.

Eg. Lead-acid batteries, Nickel-cadmium cell, Lithium- ion battery.

#### **Requirements of Primary Battery:**

- Compact, lightweight and must be fabricated from easily available raw materials.
- Economic and have benign environmental properties
- Should have a high energy density, longer shelf life
- Provide constant voltage and should have a long discharge period

#### **Requirements of Secondary Battery**

- Long shelf-life in both charged & discharged conditions
- Longer cycle life and design life
- High power to weight ratio
- Short time for a recharge.
- High voltage & high energy density

### **BASIC PRINCIPLE BEHIND BATTERY OPERATION**

The basis for a battery operation is the exchange of electrons between two chemical reactions, an oxidation reaction and a reduction reaction. The key aspect of a battery which differentiates it from other oxidation/reduction reactions (such as rusting processes, etc) is that the oxidation and reduction reaction are physically separated.

When the reactions are physically separated, a load can be inserted between the two reactions. The electrochemical potential difference between the two batteries corresponds to the voltage of the battery which drives the load, and the exchange of electrons between the two reactions corresponds to the current that passes through the load. The components of a battery, which are shown in the figure below, and consist of an electrode and electrolyte for both the reduction and oxidation reaction, a means to transfer electrons between the reduction and oxidation reaction (usually this is accomplished by a wire connected to each electrode) and a means to exchange charged ions between the two reactions.

The key components which determine many of the basic properties of the battery are the materials used for the electrode and electrolyte for both the oxidation and reduction reactions. The electrode is the physical location where the core of the redox reaction – the transfer of electrons – takes place. In many battery systems, including lead acid and alkaline batteries, the electrode is not only where the electron transfer takes place but is also a component in the chemical reaction that either uses or produces the electron. However, in other battery systems (such as fuel cells) the electrode material is itself inert and is only the site for the electron transfer from one reactant to another. For a discharging battery, the electrode at which the oxidation reaction occurs is called the anode and has a positive voltage, and the electrode at which the reduction reaction occurs is the cathode and is at a negative voltage.

## **Battery**

Batteries are devices that store energy in the form of chemical energy and convert it when required to electrical energy. Through the electrochemical reactions that occur in a battery, electrons are released and flow from one conductor (electrode) to another through external electric circuit providing an electric current that is used to do tasks. At the same time, charged ions are transported through an electrically conducting solution (electrolyte), which is in contact with the electrodes to bring the reactants to the electrode/electrolyte interface.

The electrodes and electrolyte can be made from various materials. Variations in the composition of the electrolyte and electrodes result in different electrochemical

reactions and charged ions. These influence the extent to which energy can be stored, as well as the operating voltage and performance of the battery.

A battery can be comprised of one or more electrochemical cells. An electrochemical cell consists of two electrodes or metallic conductors, in contact with an electrolyte, an ionic conductor. An electrode and its electrolyte comprise an electrode compartment. The two electrodes may share the same compartment. If the electrolytes are different, the two compartments may be joined by a salt bridge, which is a tube containing a concentrated electrolyte solution in agar jelly that completes the electrical circuits and enables the cell to function. So an electrochemical cell can be defined as a single arrangement of two electrodes in one or two electrolytes which converts chemical energy into electrical energy or electrical energy into chemical energy. Electrochemical cells can be classified into two types:

- **Galvanic Cells**
- **Electrolytic Cells**

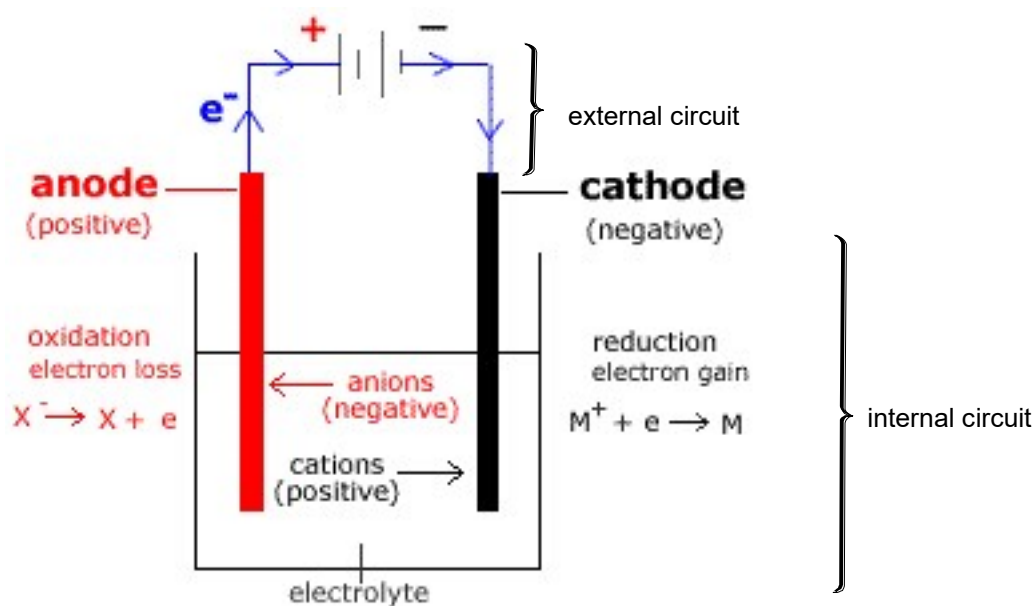


Fig.1 A schematic diagram of Electrochemical Cell

### Galvanic Cells

A galvanic cell is an electrochemical cell that produces electricity as a result of the spontaneous redox reaction occurring inside it. Galvanic cell generally consists of two electrodes dipped in two electrolyte solutions which are separated by a porous diaphragm or connected through a salt bridge. It is a single arrangement of two electrodes in one or two electrolytes which converts stored up chemical energy in the form of electroactive materials (anode & cathode

active materials) directly into electrical energy. The negatively charged electrons flow from anode to cathode and are attracted to the positive cathode through the external circuit.

### Anode vs. Cathode:

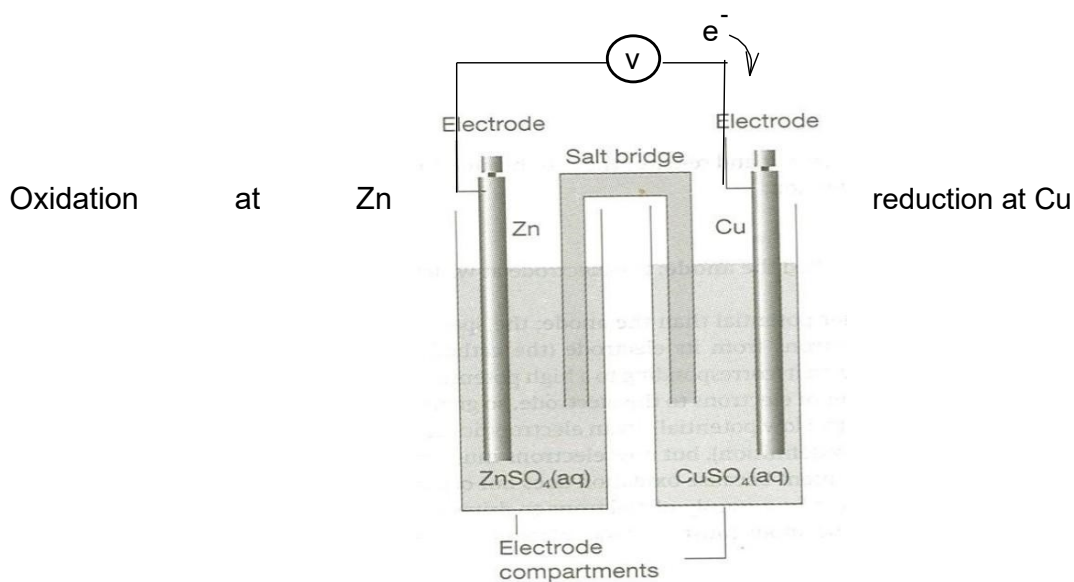
## Anode ;

- the electrode at which oxidation occurs
- is where electrons are produced
- is what anions migrate towards
- has a -ve sign.

### Cathode ;

- the electrode at which reduction occurs
- is where electrons are consumed
- is what cations migrate towards
- has a +ve sign

A typical galvanic cell can be illustrated by Daniel cell (Fig. 1.1.1)



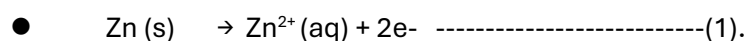
Half cell I (Anode compartment)

Half cell II (Cathode compartment)

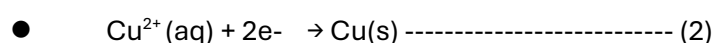
Fig.2. A schematic diagram of Daniel cell

A Daniel cell consists of two compartments, one of which contains zinc rod dipped in zinc sulphate solution and the other with a copper rod dipped in a copper sulphate solution. The

two electrolytes are connected by a salt bridge. When the zinc and copper rod electrodes are connected externally through a voltmeter by using a wire, the following oxidation-reduction reactions taking place at the electrodes. At the zinc electrode, zinc goes into the solution as  $\text{Zn}^{2+}$  ions, liberating two electrons. In the process zinc undergoes oxidation liberating two electrons. The positive ion flows from the salt bridge to the cathode and the zinc electrode becomes lighter.



At the copper electrode reduction of  $\text{Cu}^{2+}$  ions takes place with the deposition of metallic copper on the copper rod, by consuming two electrons. The negative ions flow from salt bridge to anode and copper electrode becomes heavier. The ionic conduction in the solution is coupled to the electronic conduction in the electrodes.



Each of these reactions is known as half cell reaction. The reaction (1) in which loss of electrons takes place is called oxidation half reaction; while the reaction 2, in which gain of electrons takes place, is called reduction half reaction. The net reaction is obtained by adding reactions 1 and 2. i.e.  $\text{Zn(s)} + \text{Cu}^{2+} (\text{aq}) \rightarrow \text{Zn}^{2+} (\text{aq}) + \text{Cu(s)}$  is called redox or oxidation – reduction reaction. When the circuit is closed, the electrons flow from zinc to copper through the external wire to feed the  $\text{Cu}^{2+}$  ions in the process of discharging copper and thus electrical energy or current is produced which may be used for the purpose of external work.

As in the case of Daniel cell, by the combination of any two different electrodes materials one can construct a galvanic cell. The electrode with a greater tendency to go into the solution by liberating electrons acts as an anode, & the other one with more tendency to undergo reduction acts as a cathode. In a galvanic cell anode is negative and the cathode is positive. The reason to this nomenclature is that oxidation is accompanied by the liberation of electrons which are given up to that electrode which thereby acquires a negative charge. Reduction on the other hand, is accompanied by absorption of electrons by reactant in solution from the electrode, which thereby acquires a positive charge. Hence the flow of electrons is from the negative electrode to positive electrode and the direction of flow of positive electricity, which is known as conventional current, is from the cathode to anode.

#### Electrolytic cells

An electrolytic cell is an electro –chemical cell in which a non- spontaneous reaction is driven by an external source of current although the cathode is still the site of reduction, it is now the negative electrode whereas the anode, the site of oxidation is positive.

The electrolytic cell (Fig.1.1.2) find wide applications in the purification of metals & also in electro deposition of a metal on to the surface of another metal, alloy or any conductor in general, by the process of electrolysis.

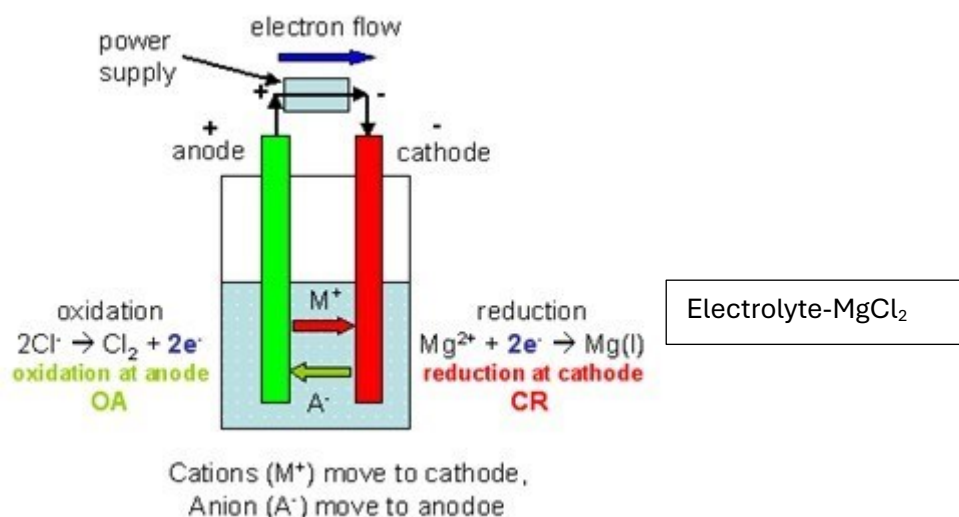


Fig.3 Schematic diagram of an electrolytic cell

Electrolysis involves the conversion of electrical energy into chemical energy i.e. chemical changes are brought about by the expense of electrical energy. Since electrolysis is a non spontaneous process, the minimum energy required to carry out such a process is equal to the free energy increase accompanying the change, & this is equal but opposite in sign to the free energy decrease accompanying the reverse spontaneous process. This is true when electrolysis is carried out reversibly. However, in irreversible conditions, the potential to be applied for electrolysis is higher than the reversible emf of the cell.

### Representation of a galvanic cell

According to the present convention, a galvanic cell is represented by keeping in view the following points:

1. The anode is written on the left hand side and the cathode is written on the right hand side of cell representation.
2. The anode is written by writing the metal (or solid phase) first and then the electrolyte along with the concentration in the bracket. The two are separated by a vertical line or a semicolon. The electrolyte may be represented by the formula of the whole compound or by ionic species.

Anode representation

Metal/ Metal ion (concentration) i.e.  $M/M^{n+}(c)$

$Zn|Zn^{2+}$  or  $Zn; Zn^{2+}$  or  $Zn|ZnSO_4(1M)$  or  $Zn; ZnSO_4(1M)$

- The cathode of the cell is represented by metal ion first and then the metal (or solid phase) thereafter. The two are separated by a vertical line or a semicolon.

Cathode representation:

$M^{n+}(c) / M$  i.e. Metal ion (concentration) / Metal

e.g.  $Cu^{2+} | Cu$  or  $Cu^{2+}; Cu$  or  $Cu^{2+}(1M); Cu$  or  $CuSO_4(1M)/Cu$

- A salt bridge is indicated by two vertical lines, separating the two half-cells. Thus the Daniel cell, may be represented as:

$Zn | ZnSO_4(1M) || CuSO_4(1M)/Cu$

$Cu(s) / Cu^{2+}(aq) || Ag^+(aq) / Ag(s)$

## Comparisons of Galvanic and Electrolytic cells

Galvanic Cell	Electrolytic Cell
Cell reaction is spontaneous	Cell reaction is non-spontaneous
Converts chemical energy to electrical energy	Converts electrical energy into chemical energy
Anode is negative and cathode is positive	Anode is positive and cathode is negative
Usually have two electrodes and two electrolytes	Single electrolyte and two electrodes
Used as a potable source of electrical energy in cars, flashlights and calculators	Used for electrolysis apparatus like electroplating and electrorefining
Example. Daniel cell	Example. Electroplating of nickel

Typically, the anode and cathode are made of different types of chemical compounds or metals. The electrolyte is a medium that allows the charged ions to be transported toward the electrodes. In fact, the flow of positive charged ions through the electrolyte balances the movement of negative electrons which makes the battery cell electrically neutral during its operation. Also, a porous and electronically insulating separator is often used between the anode and cathode to improve the mechanical strength of the electrolyte and reduce the risk of an internal short circuit. Typically, separators have a high ionic conductivity and provide electronic insulation. The current collectors can also provide



efficient transfer of electrons and remove heat from the electrodes. Thin foils of aluminium or copper are typically used as current collectors.

### **Electromotive force**

Electricity cannot flow from one electrode to another unless there is a potential difference between the two points. The difference of potential, which causes a current to flow from the electrode at higher potential to an electrode at lower potential is called the “electromotive force”(e.m.f.) of the cell “or the “cell potential” and is expressed in volts V. The emf of a cell is denoted by  $E_{\text{cell}}$ . Mathematically,

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

The driving force that pushes the negatively charged electrons away from the anode and pulls them towards the cathode is known as emf. The  $E_{\text{cell}}$  depends on the nature of the electrodes composition, (combination of electrodes, strong tendency to lose or gain electrons produces large cell potential) temperature ( $E \propto T$ ) and concentration of the electrolyte solutions. To facilitate comparison of different galvanic cells, their standard emf, denoted by  $E^{\circ}_{\text{cell}}$  is used. Standard emf of a cell is defined as the emf of a cell when the reactants & products of the cell reaction are at a unit concentration or unit activity, at 298 K and at 1 atmospheric pressure including pure solids and liquids.

The emf of a cell represents the driving force of a cell reaction. As represented by the thermodynamic relation,

$$\Delta G = -nFE$$

Where  $\Delta G$  is the free energy change accompanying a cell reaction,  $n$  is the number of electron transfer during the cell reaction, and  $F$  is the Faraday constant,  $F = eN_A$ , the magnitude of the charge per mole of electrons. Hence the above equation is the key connection between the electrical measurements on the one hand and thermodynamic properties on the other.

The cell reaction is spontaneous or feasible when  $\Delta G$  is negative.  $\Delta G$  can be negative only if the emf of the cell is positive, because, the other two factors,  $n$  &  $F$  are always positive. Thus emf of a galvanic cell is always positive. The positive emf value indicates the spontaneity of cell reaction in the given direction. When the cell potential is large, a given number of electrons traveling between the electrodes can do a large amount of electrical work. When the cell potential is small, the same number of electrons can do only a small amount of work. A cell in which the overall reaction is at equilibrium can do no work, and then the cell potential is zero.

The greater the difference, the greater is the cell potential, and the higher is the voltage. A practical way to measure the electrical potential of an electrode (cathode or anode) is to assign zero for the electrical potential of the reaction that occurs at the electrode and then use it as a reference electrode.

#### Standard electrode potential:

Standard electrode potential is the electrode potential when the electrode is in contact with a solution of unit concentration at 298 K involving pure solids and liquids. If the electrode involves a gas, then the gas is at 1 atmospheric pressure. It is denoted by  $E^\circ$ . When elements are arranged in increasing order (downwards) of their standard electrode potential, a series called electrochemical series is obtained. In a cell, the electrode with lower electrode potential has less tendency to undergo reduction and it acts as anode similarly electrode with higher electrode potential has higher tendency to undergo reduction and acts as cathode.

Reducing agents	Stable ions	Electrode half reaction $E^\circ$ volts
Lithium	$\text{Li}^+$	-3.03
Potassium	$\text{K}^+$	-2.92
Aluminium	$\text{Al}^{3+}$	-1.66
Zinc	$\text{Zn}^{2+}$	-0.76
Iron	$\text{Fe}^{3+}$	-0.44
Lead	$\text{Pb}^{2+}$	-0.13
$\text{H}_2$	$2\text{H}^+$	0
Copper	$\text{Cu}^{2+}$	0.34
Silver	$\text{Ag}^+$	0.80
Gold	$\text{Au}^{3+}$	1.52

Fig. 1.3.2. Selected standard electrode potentials

### Nernst equation

Nernst equation is an expression of a quantitative relationship between electrode potential/cell potential and concentration of the electrolyte species in an electro-chemical reaction. i.e. mathematical expression that relates the potential of an electrode to the concentrations of those species in solution that are responsible for the potential. Consider a general redox reaction:  $\text{M}^{n+}(\text{aq}) + n\text{e}^- \rightleftharpoons \text{M}(\text{s})$

$$E = E^\circ + \frac{2.303RT}{nF} \log [\text{M}^{n+}]$$

E= Electrode potential at some moment in time

$E^0$ = Standard electrode potential

R= Universal gas constant (joules per mol per K)

T= Temperature in Kelvin scale F= Faraday constant (96,500 Coulombs)

n = Number of electrons transferred in the half reaction/ cell reactions

$[M^{n+}]$ = Concentration of metal ion at that moment in time (moles per litre).

At 298 K, when the values of R.T and F are substituted, the equation reduces to,

$$E = E^0 + (0.0592/n) \log [M^{n+}]$$

This expression is known as the Nernst equation for electrode potential at 298 K. From these equations, it is clear that,

- i) If the concentration of the solution ( $M^{n+}$ ) is increased, the electrode potential increases and vice versa.
- ii) If the temperature is increased, the electrode potential increases and vice versa.

The Nernst equation can also be applied for the calculation of emf of a cell. Consider the cell reaction  $aA + bB \rightleftharpoons cC + dD$

The Nernst equation for the emf of the cell is

$$E_{\text{cell}} = E^0_{\text{cell}} - 2.303RT/nF \log [C]^c [D]^d / [A]^a [B]^b$$

At 298 K,

$$E_{\text{cell}} = E^0_{\text{cell}} - (0.0591/n) \log [C]^c [D]^d / [A]^a [B]^b$$

Where n is the number of electrons transferred during the cell reaction and  $E^0_{\text{cell}}$  is the standard emf of the cell.

### Numericals

**. Using the electrochemical series, calculate the emf of the cell  $\text{Fe(s)} / \text{Fe}^{2+}_{(0.1 \text{ M})} \parallel \text{Cd}^{2+}_{(0.2 \text{ M})} / \text{Cd}$  at 298 K. Write the cell reactions.**

**From the series we have;**

$$E^0_{\text{Cd}^{2+}/\text{Cd}} = -0.40 \text{ V} ; E^0_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$$

**At anode  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2 \text{e}^-$**

**At Cathode  $\text{Cd}^{2+} + 2 \text{e}^- \rightarrow \text{Cd}$**

**Net reaction:  $\text{Fe} + \text{Cd}^{2+} \rightarrow \text{Fe}^{2+} + \text{Cd}$**

**EMF of the cell at 298 K is given by**

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= -0.40 - (-0.44)$$

$$= 0.04 \text{ V}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591 / n) \log [\text{Fe}^{2+}] / [\text{Cd}^{2+}]$$

$$= 0.04 - (0.0591 / 2) \log [0.1] / [0.2]$$

$$= 0.0488 \text{ V}$$

## **ELECTROLYTES**

The electrolyte can be a liquid, solid, polymer, or composite (hybrid) depending on the type of battery. The electrolyte should have a high ionic conductivity, no electric conductivity, nonreactivity with the electrode materials and a wide operating temperature range. The traditional liquid electrolyte generally has a low viscosity, high energy density, high charge/discharge rate capability, a relatively low operational temperature (between  $-40^\circ\text{C}$  and  $60^\circ\text{C}$ ) and low flammability. The polymeric electrolyte can be either a gel or a solid. The solid polymeric electrolyte has the advantageous of high flexibility, high energy density, multifunctional applications, good safety and mechanical properties and thermal/chemical stability. But solid polymeric electrolytes typically have low ionic conductivities at room temperature ( $10^{-5} - 10^{-1} \text{ mS cm}^{-1}$ ). Gel polymeric electrolytes, on the other hand, have relatively high ionic conductivities ( $1 \text{ mS cm}^{-1}$ ), high flexibility, multifunctional applications, and chemical stability, but they have poor mechanical strength and poor interfacial properties. The main advantages of a solid polymeric electrolyte are no electrolyte leakage, high safety (nonflammability), nonvolatility, thermal and mechanical stability, ease of fabrication, and high achievable power density and cyclability.

**Energetic of cell reactions:**

### **The relation between E and ΔG:**

$$\Delta G = -nFE$$

### **Relation between E and ΔH**

$$\text{Enthalpy Change } \Delta H = nF[T(\delta E/\delta T)_p - E] \text{ -----(5)}$$

If we know emf and temperature coefficient of emf, ΔH can be calculated..

### **Relation between E and ΔS :**

$$\Delta S = nF(\delta E/\delta T)_p \text{ -----(6)}$$

## **KEY BATTERY PERFORMANCE METRICS**

The characteristic performance of a battery determines its suitability for the desired application. Some of them are –

### **a. Current:**

Current is a measure of the rate of flow of electrons during discharge. It is the amount of charge flowing per unit time and is expressed in ampere (coulomb per second). For uniform current, electrolyte of high conductance is desirable. Batteries provide direct current.

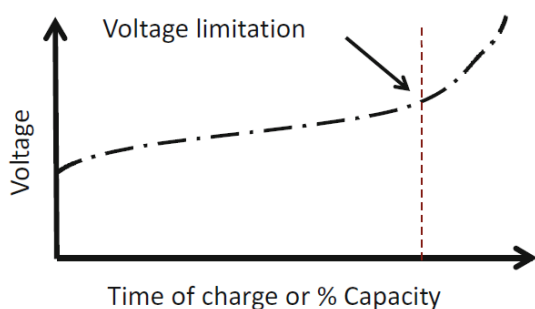
### **b. Capacity:**

Capacity is the charge in ampere hours (A h) that could be obtained from the battery.

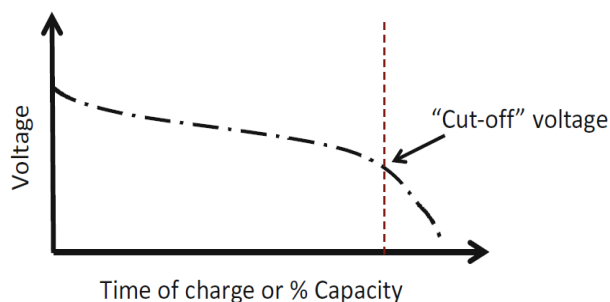
This depends on the size of the battery and is determined by the Faraday relation,

$$C = \frac{m \times n \times F}{M}$$

Where C is the capacity in A h, m is the mass of active material and M is the molar mass.



**Fig 2:** Battery voltage during charging



**Fig 3:** Battery voltage during discharging

The amount of active materials consumed during discharge determines the capacity of the battery. The capacity also depends on the discharge conditions. It is measured by

finding the time 't' taken for the battery to reach a minimum voltage,  $E_{\text{cell}}^{\text{min}}$  for a fixed current discharge (i amperes). (The cell is said to be dead at minimum voltage). A plot of time against voltage at a fixed current discharge is shown in Fig. 5 and 6 The length of the flat portion of the curve is a measure of the capacity of the battery, the longer the flat portion better the capacity.

**c. Electricity Storage Density:**

Electricity storage density is a measure of the charge per unit mass stored in the battery, The mass of the battery includes masses of the electrolyte, current collectors, terminals, the case, and other subsidiary elements. To get high storage density the mass of subsidiary elements should be minimum. For instance, 7g of lithium is required at anode to give 96500 C whereas, for the same charge, 65g of zinc would be required.

**d. Energy Efficiency:**

Energy efficiency for a storage battery is given by -

% Energy efficiency

$$= (\text{Energy released on discharge} / \text{Energy required for charging}) \times 100$$

Energy efficiency depends on the current efficiency of the electrode processes, the overpotentials during discharge and charge, and internal resistance. A battery should have high energy efficiency.

**e. Cycle Life:**

The cycle life of a battery is the number of charge-discharge cycles that can be achieved before failure occurs. (Note that cycle life applies to secondary batteries). It is necessary that during charging the active material is regenerated in a suitable state for discharge. The discharge-charge cycle depends on chemical composition, morphological changes, and distribution of active materials in the cell.

The cycle life of a battery is affected by corrosion at contact points, shedding of the active material from the plates, and shorting between the electrodes due to irregular crystal growth and changes in morphology.

**f. Shelf Life**

Shelf life is the period of storage under specified conditions during which a battery retains its performance level. Shelf life is affected by self-discharge. Self-discharge

occurs when there is a reaction between the anode and the cathode active materials or corrosion of current collectors.

In addition, a commercial battery should have tolerance to service conditions such as variation in temperature, vibration and shock, and should have reliable output.

**g. Energy Density:**

Energy density is the ratio of the energy available from a battery to its mass (or volume) (Wh/Kg) or Wh/L.

Energy density is determined by measuring the capacity and recording the average voltage (voltage averaged during the discharge) and the total mass (or volume) of the battery. A battery should have continuous energy density above a certain value or a very high energy density for a short period.

**h. Power Density:**

Power density is the ratio of the power available from a battery to its mass (W/kg) or volume (W/L). A battery should have continuous power density above a certain value or a high value for a short period

## **EMERGING BATTERY TECHNOLOGIES**

Emerging battery technologies are constantly developing to fulfil the increasing requirements of many industries, such as consumer electronics, electric vehicles (EVs), renewable energy storage, and grid stability. Presented below are many noteworthy developing battery technologies:

**a. Solid-State Batteries:** These batteries substitute the liquid or gel electrolyte present in conventional lithium-ion batteries with a solid electrolyte, resulting in increased energy density, enhanced safety, and perhaps extended longevity. The improved energy density and lower fire danger of solid-state batteries are expected to bring about a revolution in electric vehicles (EVs) and portable gadgets.

**b. Lithium-Sulfur Batteries:** Lithium-sulfur batteries possess the capacity to provide greater energy density in comparison to lithium-ion batteries. They employ sulfur as the cathode material, which is abundant and affordable, resulting in the possibility of reduced production expenses. Nevertheless, there are still unresolved issues that

need to be tackled, such as the low electrical conductivity of sulfur and the dissolution of polysulfides.

- c. Lithium-air batteries:** Lithium-air batteries have an exceedingly elevated theoretical energy density, with the potential to surpass even that of gasoline. The anode is composed of lithium metal, while the cathode is made up of oxygen obtained from the air. Nevertheless, it is necessary to address practical obstacles such as the restricted number of cycles that lithium metal anodes may undergo and concerns over their stability.
- d. Flow Batteries:** Flow batteries utilize liquid electrolytes stored in separate external tanks to store energy, providing the advantages of scalability and flexibility in terms of capacity. Vanadium redox flow batteries (VRFBs) are now the most prominent form. However, continuing research aims to investigate other chemistries that can provide better energy density and cheaper prices.
- e. Metal-Air Batteries:** Metal-air batteries, such as zinc-air and aluminum-air batteries, employ a metal anode and oxygen derived from the atmosphere as the cathode. These materials have large theoretical energy densities and may be inexpensive since their component materials are abundant. Nevertheless, the issues concerning reversibility, efficiency, and cycle life must be resolved to achieve commercial feasibility.
- f. Sodium-Ion Batteries:** Sodium-ion batteries are being investigated as a more economical substitute for lithium-ion batteries, capitalizing on the ample availability of sodium minerals. Although they generally have lower energy density than lithium-ion batteries, they show potential for use in stationary energy storage applications that emphasize cost-effectiveness above energy density.

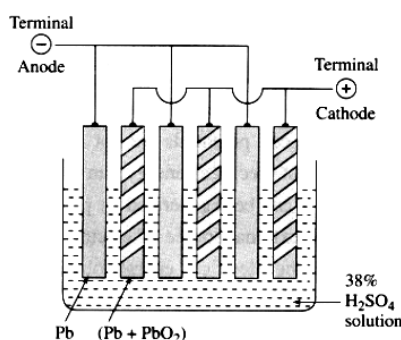
These nascent battery technologies are at different phases of advancement, spanning from initial investigation to commercial implementation. Ongoing research and innovation in battery technology are essential for tackling difficulties and fully harnessing their capacity to fuel the future.

**Lead Acid Battery/Storage Battery** (Lead Accumulator or Car Battery or the acid battery)

**Construction:** The electrodes are lead grids. Grids are used to maximize the surface area. The anode grid is filled with finely divided spongy lead (Pb) and the cathode grid is packed with lead dioxide (PbO<sub>2</sub>). Both electrodes are submerged in a sulfuric acid

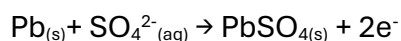
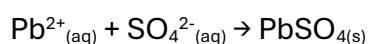
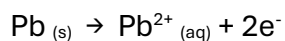


solution ( $\text{H}_2\text{SO}_4$ ) having a specific gravity of about 1.25 that acts as the electrolyte. The anode and cathode grids are separated by insulators like strips of wood, rubber, or glass fiber. The battery is encased in a plastic container or hard vulcanized rubber vessel. The cell doesn't need separate anode and cathode compartments because the oxidizing and reducing agents are both solids ( $\text{PbO}_2$  &  $\text{Pb}$ ) that are kept from coming into contact by insulating spacers between the grids. Both anode and cathode are immersed in a common electrolyte (i.e. cell without liquid junction). This is an example of a **wet cell** because the electrolyte is an aqueous sulphuric acid solution.

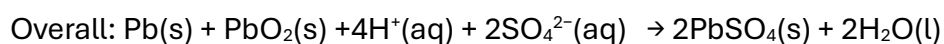
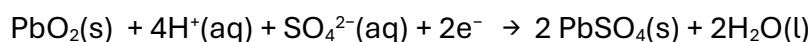
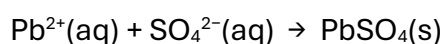
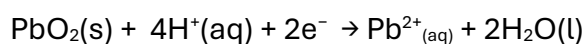


### Discharging reactions

At the anode



At the cathode:

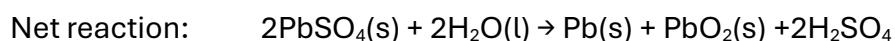
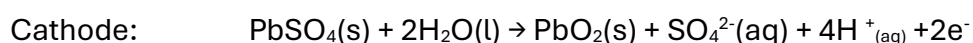
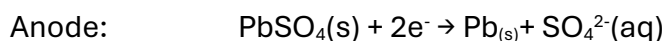


**Explanation:**

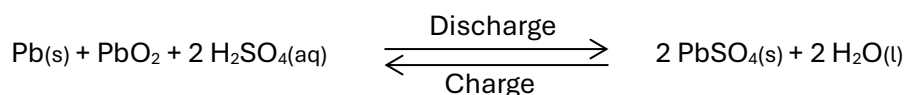
At the anode, lead atoms lose two electrons ( $e^-$ ) and become positively charged lead ions ( $Pb^{2+}$ ). The lead ions combine with the sulfate ions ( $SO_4^{2-}$ ) in the sulfuric acid solution to produce lead sulfate ( $PbSO_4$ ).

At the cathode, lead dioxide gains electrons, releasing oxygen, which attaches to hydrogen ions ( $H^+$ ) to produce water ( $H_2O$  (l)) and lead ions. The lead ions react with sulfate ions to produce lead sulfate. As this reaction progresses, the flow of electrons creates an electric current. Lead sulfate adheres to each electrode and water increases. The concentration of sulfuric acid decreases and the amount of lead and lead dioxide decreases. When the reactants are depleted, the battery stops producing electricity. The reaction can be reversed by recharging the battery & the  $PbSO_4$  formed during discharge remains adhered to each electrode and is available at the site during recharging. The nominal voltage of each cell is about 2.1 V. The lead storage battery is designed to operate reversibly so that it can be used for storing electrical energy. They are called storage batteries because their essential function is to store electrical energy. It is used to store energy in chemical form.

### **Reactions during Charging:**



Recharging is possible because  $PbSO_4$  formed during discharge adheres to the electrodes. By attaching an external power source to a battery (>2 volts), a current runs through the poles in the opposite direction from normal discharge. This changes the lead sulfate and water back into the original reactants, lead dioxide and sulfuric acid, i.e. the electrodes return to their former composition and the sulfuric acid is regenerated. Charging, therefore, produces a gradual increase in sulfuric acid concentration. Since the level of charge on a storage battery is related to sulfuric acid concentration, the specific gravity of the ( $H_2SO_4$ ) solution is a measure of the operational condition of a battery. A charged battery at room temperature with its electrolyte at normal concentration supplies a potential difference of 2.1 to 2.2 V. The complete reaction cycle of a lead acid storage battery is as follows.



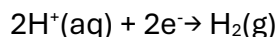
In an automobile, the energy necessary for recharging the battery is provided by the generator driven by the engine. As the external source forces electrons from one electrode to another, the  $\text{PbSO}_4$  is converted to Pb at one electrode and  $\text{PbO}_2$  at the other.

### **Overcharging:**

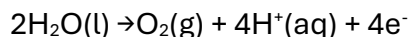
Electrolysis of water: The net reaction can be summarized by the equation.



No gases will be liberated during charging if lead ions are present in the solution. If the electrolysis is permitted to proceed further, hydrogen gas is formed at the cathode, and oxygen gas is evolved at the anode. The hydrogen ions are discharged at the cathode through the reaction.



Sulphate ions are resistant to oxidation and are not discharged at the cathode. Water is oxidized at the anode in preference to  $\text{SO}_4^{2-}$



Consequences: (i) Excessive charging may reduce the acid level and may damage the exposed electrode grids (ii) In extreme cases, there will be dangerous high-pressure build-up that can lead to a serious risk of explosion. In more normal circumstances, the older version of the battery needs to be ‘topped up’ from time to time.

Recent years have seen the introduction of “maintenance-free batteries” without a gas-release vent. Here the gassing is controlled by careful choice of the composition of the lead alloys used i.e. by using a Pb-Ca (0.1 %) as the anode which inhibits the electrolysis of water.

Alternatively, some modern batteries contain a catalyst (e.g. a mixture of 98% ceria (cerium oxide) & 2% platinum) that combines the hydrogen and oxygen produced during discharge back into the water. Thus, the battery retains its potency and requires no maintenance. Such batteries are sealed as there is no need to add water and this sealing prevents leakage of cell materials.

Applications: Many battery designs are available for a wide variety of uses that can be classified into three main categories. (a) Automotive (b) Industrial & (c) Consumer batteries.

The automotive type is used in cars and trucks, to provide a short burst of power for starting the engine. It is incorporated as an essential accessory into the starting circuit of internal combustion engines for starting, lighting & ignition (SLI). The industrial batteries are used for heavy-duty applications such as motive and standby power. This class of batteries is used to operate electric trucks, submarines, and mine locomotives. They also provide power for the air conditioning and lighting systems. It is used in stationary backup power applications such as telecommunication systems, to ensure that, for example, the telephone network will continue to operate even in the event of a mains power failure. Such batteries are kept in hospital operating theaters, railway signal centers, and other places where a power failure might be disastrous and is used to supply electrical power during emergencies. The consumer batteries are used in emergency lighting systems, security and alarm systems, public address systems, power tools, UPS in computers, and vehicles.

**Advantages:**

- A lead storage battery is highly efficient. The voltage efficiency of the cell is defined as follows.
- Voltage efficiency = 
$$\frac{\text{average voltage during discharge}}{\text{average voltage during charge}}$$
- The voltage efficiency of the lead–acid cell is about 80 %.
- The near reversibility is a consequence of the faster rate of chemical reactions in the cell, i.e. anode oxidizes easily, and the cathode reduces easily leading to an overall reaction with a high negative free energy change.
- A lead – acid battery provides a good service for several years. The number of recharges possible ranges from 300 to 1500, depending on the battery’s design and conditions. The sealed lead-acid batteries can withstand up to 2000 – recharging. The time required for recharging is relatively low i.e about 2-8 hours.
- The battery has low internal self–discharge.

- A typical car battery provides a voltage of 12 V. This is not a large voltage, but the battery can provide a large current. E.g. over 10 A, without being destroyed.

**Disadvantages:**

- If left unused in partially charged condition, it can be ruined in a short time by nucleation and the growth of relatively large  $\text{PbSO}_4$  crystals, which are not easily reduced or oxidized by the charging current. This disaster is known as 'sulfation'.
- The lead acid battery has low energy storage to weight ratio i.e. its chief disadvantage is its great weight. (energy density  $\sim 35 \text{ wh / kg}$ )
- The cell potential decreases with a decrease in concentration of sulfuric acid. During the discharge process sulfuric acid is consumed and water is produced. So, the solution of sulfuric acid in the cell becomes less concentrated. The state of charge of the cell can be judged by the concentration of sulfuric acid in the liquid and this is usually done with a simple device to measure the density of the liquid. The density of a healthy, fully charged battery is  $\geq 1.25 \text{ g/mL}$ .
- The battery is not efficient at a lower temperature. For a battery to function properly, the electrolyte must be fully conducting. There will be an increase in the viscosity of the electrolyte due to a decrease in the temperature. This leads to a decrease in cell potential.
- Overcharging may damage the exposed electrodes and may also lead to an explosion in extreme cases. Sulfuric acid is a highly corrosive liquid. In the event of an explosion, the electrolyte is sprayed on to the individual who is working on the battery. Therefore, safety goggles must be worn when working with these batteries.
- Lead is toxic and hence environmental & health problems arise due to careless disposal by consumers.
- The corrosion of the lead grid at the lead dioxide electrode is one of the primary causes of lead acid battery failure.

**Nickel-Metal Hydride (NiMH) battery:**

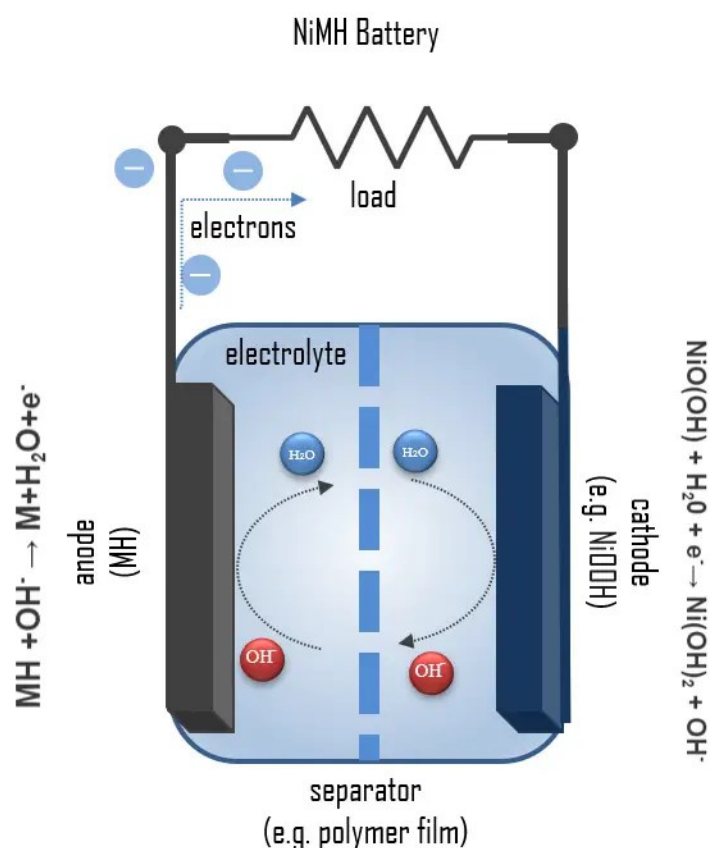
As electronic products have come to feature more sophisticated functions, more compact sizes, and lighter weights, the sources of power that operate these products

have been required to deliver increasingly higher levels of energy. To meet this requirement, nickel-metal hydride batteries have been developed and manufactured with nickel hydroxide for the positive electrode and hydrogen absorbing alloys, capable of absorbing and releasing hydrogen at high-density levels, for the negative electrode. Because NiMH batteries have about twice the energy density of Ni-Cd batteries and a similar operating voltage as that of Ni-Cd batteries, they have become a mainstay in rechargeable batteries.

### **Construction**

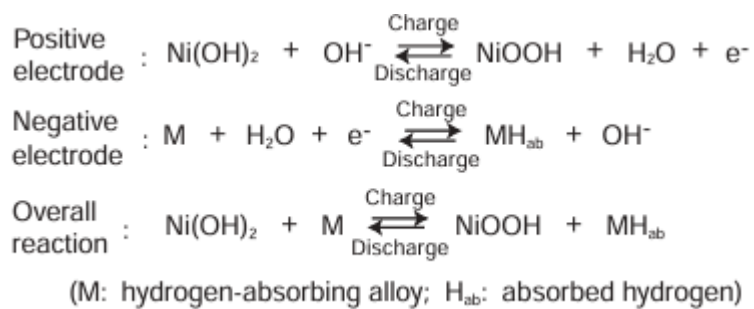
Nickel-metal hydride batteries consist of a positive plate containing nickel hydroxide as its principal active material, a negative plate mainly composed of hydrogen-absorbing alloys, a separator made of fine fibers, an alkaline electrolyte, a metal case, and a sealing plate provided with a self-resealing safety vent. Their basic structure is identical to that of Ni-Cd batteries. With cylindrical nickel-metal hydride batteries, the positive and negative plates are separated by the separator, wound into a coil, inserted into the case, and sealed by the sealing plate through an electrically insulated gasket.

### **Structure of Nickel-Metal Hydride Batteries**

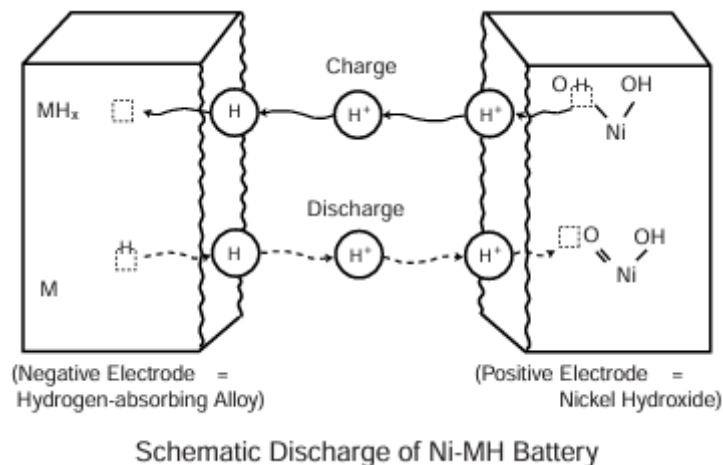


Hydrogen-absorbing alloys have a comparatively short history which dates back about 20 years to the discovery of NiFe, MgNi and LaNi<sub>5</sub> alloys. They are capable of absorbing hydrogen equivalent to about a thousand times of their own volume, generating metal hydrides and also of releasing the hydrogen that they absorbed. These hydrogen-absorbing alloys combine metal (A) whose hydrides generate heat exothermically with metal (B) whose hydrides generate heat endothermically to produce the suitable binding energy so that hydrogen can be absorbed and released at or around normal temperature and pressure levels. Depending on how metals A and B are combined, the alloys are classified into the following types: AB (TiFe, etc.), AB<sub>2</sub> (ZnMn<sub>2</sub>, etc.), AB<sub>5</sub> (LaNi<sub>5</sub>, etc.) and A<sub>2</sub>B (Mg<sub>2</sub>Ni, etc.). From the perspective of charge and discharge efficiency and durability, the field of candidate metals suited for use as electrodes in storage batteries is now being narrowed down to AB<sub>5</sub> type alloys in which rare-earth metals, especially metals in the lanthanum group, and nickel serve as the host metals; and to AB<sub>2</sub> type alloys in which the titanium and nickel serve as the host metals.

Nickel-metal hydride batteries employ nickel hydroxide for the positive electrode like Ni-Cd batteries. Hydrogen is stored in a hydrogen-absorbing alloy for the negative electrode, and an aqueous solution consisting mainly of potassium hydroxide for the electrolyte. Their charge and discharge reactions are shown below.



As can be seen by the overall reaction given above, the chief characteristics of the principle behind a nickel-metal hydride battery is that hydrogen moves from the positive to negative electrode during charge and reverse during discharge, with the electrolyte taking no part in the reaction, which means that there is no accompanying increase or decrease in the electrolyte. A model of this battery's charge and discharge mechanism is shown in the figure below.



The hydrogen-absorbing alloy negative electrode successfully reduces the gaseous oxygen given off from the positive electrode during overcharge by sufficiently increasing the capacity of the negative electrode which is the same method employed by NiCd batteries. By keeping the battery's internal pressure constant in this manner, it is possible to seal the battery.



## **Advantages of nickel metal hydride batteries**

### **1. Energy density and capacity**

NiMH batteries boast commendable energy density, surpassing traditional nickel-cadmium batteries. Their capacity ranges from approximately 1000mAh to 3000mAh or higher, providing reliable and sustained power for various devices.

### **2. Rechargeability and cycle life**

These batteries excel in longevity, enduring hundreds to thousands of charge-discharge cycles. Their rechargeability and ability to retain capacity over multiple cycles make them a cost-effective and sustainable option for numerous consumer electronics and portable gadgets.

### **3. Environmental friendliness**

Comprising fewer harmful materials compared to certain battery types, NiMH batteries present an environmentally friendly choice. The absence of toxic cadmium reduces environmental impact during disposal or recycling, aligning with eco-conscious practices.

### **4. Enhanced safety features**

Relative to some battery chemistries, NiMH batteries possess a safer profile, exhibiting stability and lower risk of thermal runaway or fire hazards. This safety factor contributes to their suitability in various applications where reliability is crucial.

### **5. Cost-effectiveness**

NiMH batteries are known for their cost efficiency. With the capability to be recharged hundreds to thousands of times before significant capacity loss, they offer a long-term economic power solution, reducing the need for frequent replacements.

## **Disadvantages of nickel metal hydride batteries**

### **1. High self-discharge rate**

A notable drawback of NiMH batteries is their relatively high self-discharge rate. They can lose around 1-5% of their charge per day when idle, affecting their shelf life and necessitating regular recharging.

## 2. Memory effect and voltage sag

While less prone than nickel-cadmium batteries, NiMH cells can still suffer from memory effect issues if not fully discharged before recharging. Moreover, they might exhibit voltage sag under heavy loads, impacting performance in devices requiring consistent power output.

## 3. Sensitivity to temperature extremes

Extreme temperatures adversely affect NiMH battery performance. High temperatures accelerate self-discharge and degrade the battery, while low temperatures reduce efficiency and capacity, limiting functionality in extreme environmental conditions.

## 4. Limited fast charging capability

NiMH batteries have slower charging rates compared to newer technologies. Their limited ability for rapid charging requires longer charging times, affecting convenience in fast-paced scenarios.

## 5. Reduced voltage output

Compared to some newer battery chemistries, NiMH batteries exhibit lower voltage outputs, affecting their compatibility with devices requiring higher voltage levels for optimal performance.

## **Applications of NiMH batteries**

NiMH batteries have found applications across various industries and consumer devices, catering to diverse power needs.

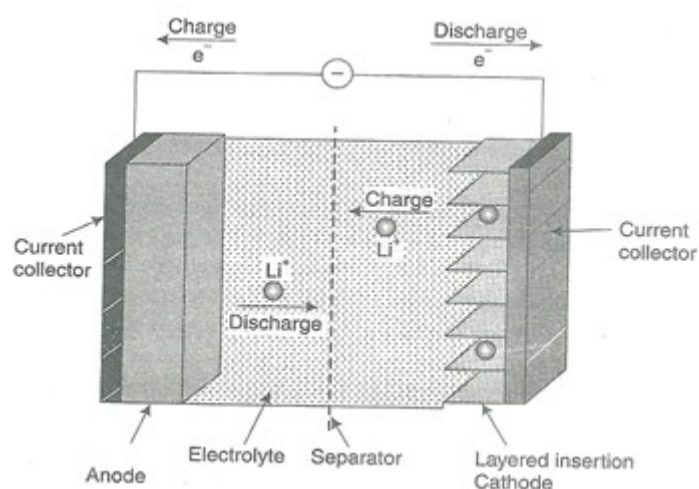
Some of the typical applications include Consumer electronics, Power tools, medical devices, Hybrid vehicles, Emergency lighting and backup power, Renewable energy storage, Flashlights and portable devices, and Electric bicycles and scooters.

## Li-Ion batteries

Li-ion batteries have revolutionized the world of portable electronics and are making significant strides in electric vehicles and grid storage.

### Construction:

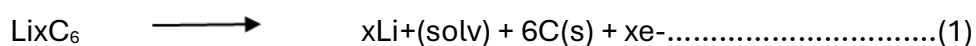
The anode is a lithium-carbide intercalate ( $\text{Li}_x\text{C}_6$ ). The cathode is a transition metal oxide  $\text{MO}_2$  of variable oxidation state ( $\text{MnO}_2$ ,  $\text{CoO}_2$ ,  $\text{NiO}_2$ ) which can intercalate lithium usually cobalt dioxide,  $\text{CoO}_2$  is used. The electrolyte is usually inert polar dry ether or carbonate (diethyl carbonate or propylene carbonate), in which a conductivity salt such as  $\text{LiPF}_6$  or  $\text{LiBF}_4$  is dissolved.



Schematic diagram of Rechargeable lithium ion battery

Working: Graphite has a layered structure and its electrochemically reduced in an aprotic organic electrolyte containing lithium salts and lithium is intercalated (or doped) between the layers of graphite to form Lithium-Graphite intercalated compound (GIC). Li-GIC undergoes oxidation leaving an electron.

At anode:

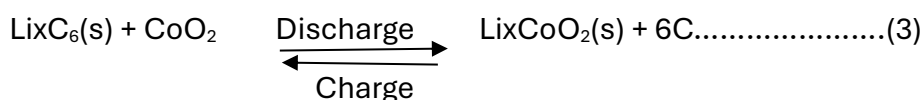


When a negative electrode is discharged, lithium is deintercalated (undoped) from lithiated graphite and lithium ions dissolve into the electrolyte. The lithium content in the  $\text{LiCoO}_2$  electrode reversibly changes during charge and discharge as indicated in the following equation:

At cathode:



Net cell reaction:



Explanations: It is called as a lithium ion battery to emphasise that it contains no lithium metal. Both the electrodes are intercalation compounds. The electrode on the left serves as the anode when the cell discharges. It is a special intercalation compound consisting of a graphite host into which lithium ions have been electrochemically inserted between the carbon atom layers. The lithiated graphite is written as  $\text{Li}_x\text{C}_6$ . During the discharge, the lithium ions are extracted by the half-reaction (1). The electrode that serves as cathode during discharge is normally cobalt dioxide. The reduction half reaction is cathode during discharge is normally cobalt dioxide. The reduction half reaction shown in eq.(2), where cobalt undergoes reduction from IV to III oxidation state. The overall reaction is shown in eq.(3). During discharge, the  $\text{Li}^+$  ions spontaneously migrate from the lithium graphite anode to the  $\text{CoO}_2$  cathode, enabling the current to flow through the external circuit. When charged, cobalt ions are oxidized and lithium ions migrate into the graphite, when discharging the battery delivers energy to the external load and when charging it receives energy from a D.C. power source. The electrode that acts as an anode, during discharging becomes a cathode when its charging.

#### Advantages

- Designed to overcome the safety problems associated with the highly reactive properties of Lithium metal.
- Long cycle life (400-1200 cycles).
- Smaller, lighter and provide greater energy density than either nickel-cadmium or nickel-metal-hydride batteries
- Can be operated in a wide temperature range and can be recharged before they are fully charged.
- Typically designed to be recharged in the device rather than in an external charger.
- The average voltage of a Li-ion battery is equivalent to three Ni-Cd cells.
- A typical Li-ion battery can store 150 watt-hours of electricity in 1 kilogram of battery as compared to lead acid batteries can store only 25 watt-hours of electricity in one kilogram.

## Limitations

- Poor charge retention
- Self discharge rate is about 10% per month
- High cost
- Traditional Li-ion batteries rely on liquid electrolytes, which are flammable and can pose a fire risk if the battery ruptures or overheats. This is where solid-state electrolytes emerge as a potential game-changer.
  - The liquid electrolytes in Li-ion batteries have the following limitations.
    - a. Flammability: In case of a battery malfunction, like overheating due to external factors or internal short circuits, these flammable organic solvents can readily ignite, leading to thermal runaway – a potentially catastrophic chain reaction.
    - b. Volatility: Liquid electrolytes are prone to evaporation at high temperatures, particularly during charging, leading to a loss of electrolyte and reduced battery performance over time.
    - c. Limited Temperature Range: The performance of liquid electrolytes deteriorates at extreme temperatures. They freeze at low temperatures, hindering ion movement and compromising battery performance. Conversely, high temperatures can accelerate solvent decomposition, impacting battery life and safety.

## **Exploring alternative batteries**

### **Sodium-ion batteries (SIBs)**

Sodium-ion (Na-ion) batteries emerge as a compelling contender, offering immense potential due to the abundant and readily available element sodium (Na).

#### 1. Sodium:

Lithium, the heart of Li-ion batteries, is a relatively rare element found in specific geological formations. Extracting and processing lithium can be energy-intensive and geographically limited, contributing to cost fluctuations. In contrast, sodium (Na) is the

sixth most abundant element in the Earth's crust, readily available in seawater and salt deposits.

Extracting sodium is a simpler and less energy-intensive process compared to lithium. This translates to a more stable and potentially lower cost for the raw material used in Na-ion batteries. This cost advantage positions sodium-ion as a potentially game-changing technology for large-scale energy storage applications.

## 2. Similarities and Differences:

**Similarities:** Lithium (Li) and sodium (Na) belong to the same group (Group 1, Alkali Metals) in the periodic table. They share similar chemical properties, readily losing their single valence electron and transforming into positively charged ions ( $\text{Li}^+$  and  $\text{Na}^+$ ). This ability to lose electrons makes them ideal candidates for battery applications.

**Ionic Radius:** A crucial difference exists in their ionic radii. Lithium ions ( $\text{Li}^+$ ) are smaller (around  $0.76 \text{ \AA}$ ) compared to sodium ions ( $\text{Na}^+$ ) (around  $1.00 \text{ \AA}$ ). This difference in ionic size has implications for how these ions interact with electrode materials in batteries.

**The Flow of Ions:** Li-ion and Na-ion batteries function based on the movement of ions between electrodes during charge and discharge cycles. However, the larger size of  $\text{Na}^+$  ions can pose a challenge for some electrode materials traditionally used in Li-ion batteries. These materials might not offer enough space for efficient  $\text{Na}^+$  ion movement, hindering performance.

## Challenges and Advancements in Na-ion Technology:

**Electrode Material Design:** The key challenge lies in creating electrode materials with structures that can efficiently accommodate the larger sodium ions. Researchers are actively exploring novel materials like Prussian blue analogues and layered sodium vanadates that show promise for improved  $\text{Na}^+$  ion mobility.

**Performance Optimization:** While advancements are being made, Na-ion batteries generally exhibit lower energy and power densities than Li-ion batteries. Ongoing research focuses on optimising electrode materials and electrolytes to enhance these performance metrics.

## Alternative energy devices

### Fuel Cells

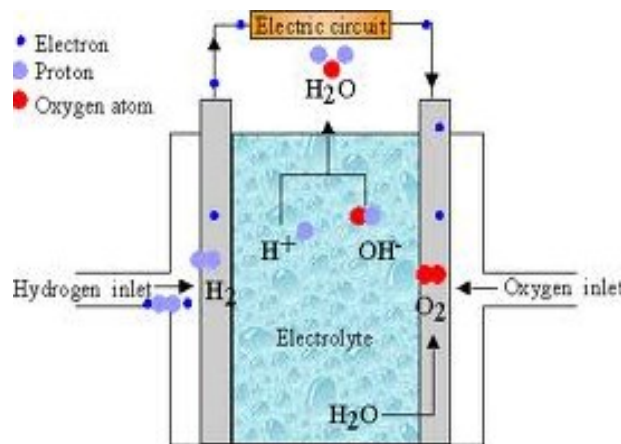
A fuel cell is a galvanic cell of a special type in which chemical energy contained in a fuel – oxidant system is converted directly into electrical energy in a continuous electrochemical process. It is an energy conversion device or electricity producer. The fuel cell has two electrodes and an electrolyte like a primary cell. The reactants (i.e. fuel + oxidant) are constantly supplied from outside and the products are removed at the same rate as they are formed.

Cell: Fuel/ electrode/electrolyte/electrode/oxidant.

Anode: Fuel + oxygen ----->Oxidation products+ ne-

Cathode: Oxidant + ne<sup>-</sup> ----->Reduction products

A fuel cell consists of fuel, electrodes, electrolyte, & oxidant. Fuel undergoes oxidation at the anode and oxidant gets reduced at the cathode. The cell can produce current as long as the reactants are supplied. Most fuel cells produce low voltages, commonly less than one volt, so a number of them are connected in series in “fuel batteries.”



**Figure 1.7** Fuel cell

Eg:- H<sub>2</sub>-O<sub>2</sub> fuel cell, CH<sub>3</sub>OH-O<sub>2</sub> fuel cell, Solid-oxide fuel cell, Molten carbonate fuel cell

### Advantages of fuel cells

- High fuel to electricity conversion efficiency of 70-75 % while a thermal power plant converts 35-40% chemical energy of coal into electrical energy.
- Fuel cell products do not cause pollution problems such as noise pollution, chemical pollution and thermal pollution normally associated with conversional power plants.
- Fuel cell power plants can be located near the point of use electricity such as on an urban location, rather than at a remote place. So transmission and distribution loss (~30%) could be avoided.
- A fuel cell will produce a steady electric current as long as fresh reactants are available.

## 1. Methanol Fuel Cells

Construction and Working

Electrolyte:- Sulphuric acid

Electrodes:- Typical gas diffusion electrodes, made up of porous C coated with Pt catalyst.

Fuel:- Methanol

Oxidant:- Air

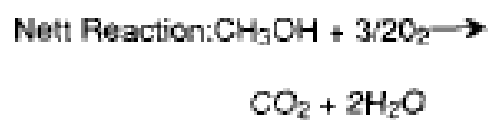
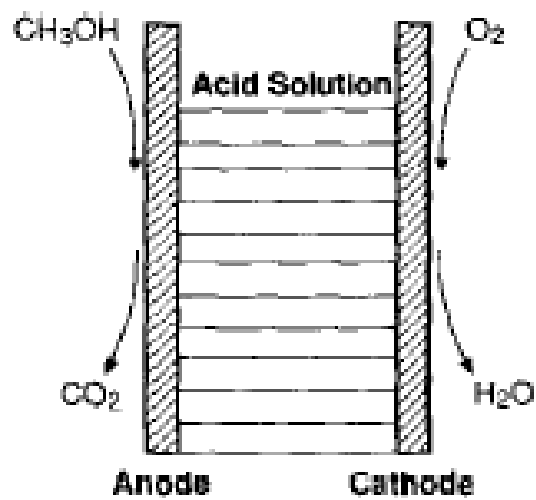
Catalyst:- Platinum

Operating temperature:- 30 – 80°C.

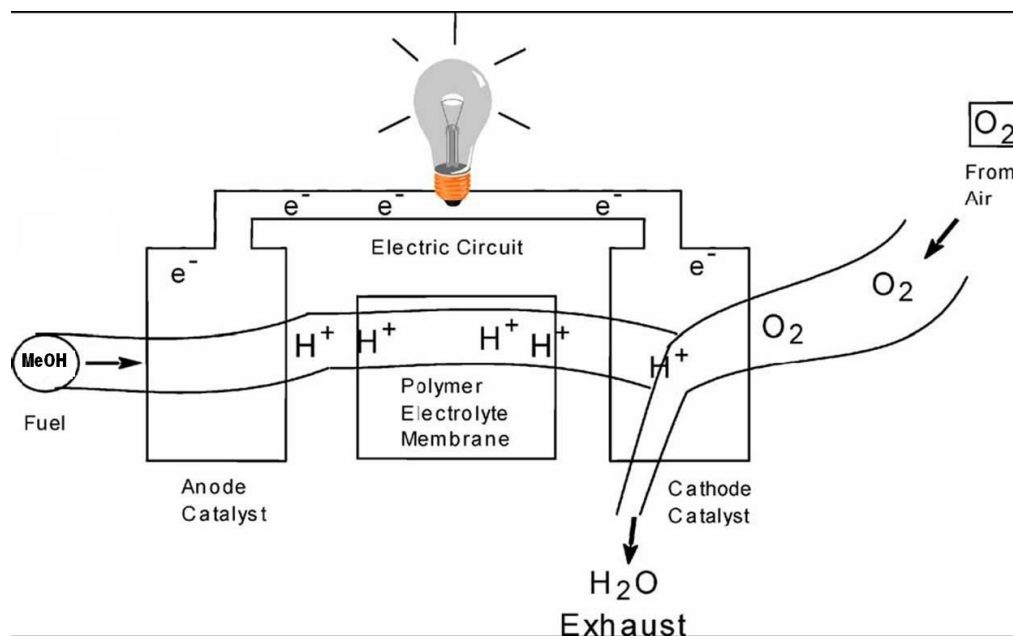
Charge-carrier:-  $H^+$

- Electrosorption (forming  $Pt-CH_2OH$ ,  $Pt_2-CHOH$  species) of methanol onto Platinum layer deposited on membrane electrode assembly (MEA)
- Addition of oxygen to adsorbed carbon-containing intermediates generating  $CO_2$





### Schematic Diagram of a Methanol Fuel Cell



### Operation of Fuel Cell

### Proton exchange membrane fuel cell (PEMFC)

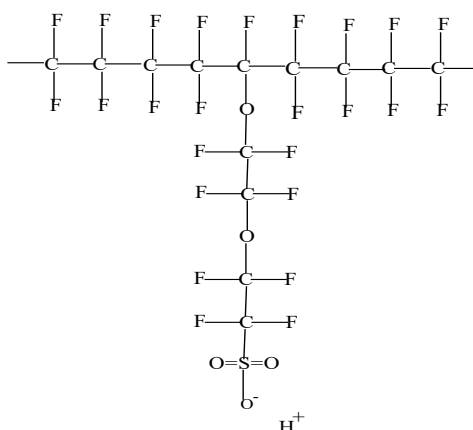
Polymer electrolyte membrane fuel cells – also called proton exchange membrane fuel cells – deliver high power density and offer the advantages of low weight and volume, compared to other fuel cells. PEM fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst. They need only hydrogen, oxygen from the air, and water to operate and do not require corrosive fluids like some fuel cells. Polymer electrolyte membrane fuel cells operate at relatively low temperatures, around 80 °C (176 °F).

Low temperature operation allows them to start quickly (less warm-up time) and results in less wear on system components, resulting in better durability. However, it requires that a noble-metal catalyst (typically platinum) be used to separate the hydrogen's electrons and protons, adding to system cost. The platinum catalyst is also extremely sensitive to CO poisoning, making it necessary to employ an additional reaction to reduce CO in the fuel gas if the hydrogen is derived from an alcohol or hydrocarbon fuel. This also adds cost. Developers are currently exploring Pt/Ru catalysts that are more resistant to CO.

***Role of Proton conducting membranes:***

- The membrane function in two ways: It acts as the electrolyte which provides ionic communication between the anode and the cathode and also it serves as the separator for the two-reactant gases.
- Optimized proton and water transport properties of the membrane and proper water management are crucial for efficient fuel cell operation.
- Dehydration of the membrane reduces the proton conductivity and excess of water can lead to the flooding of the electrolyte. Both conditions result in poor performance.

- The absence of solution-phase electrolyte in PEF fuel cells, compared to alkaline and phosphoric acid fuel cells greatly reduces the complexity of the fuel and oxidant flow controls.
- Polymeric electrolyte is carbon dioxide tolerant.
- The most important breakthrough came with the development of perfluorinated membrane by DuPont. From 1966, the membrane requirements were best met by nafion family of perfluorinated ionomer membranes. Lifetimes over 60,000 hrs have been achieved at 353 K. Their general formula is



**Construction:**

**Electrolyte:**-Ion exchange polymeric membranes. This is an excellent insulator, but an excellent conductor of H<sup>+</sup> ions. The material used, consists of a fluorocarbon polymer backbone, similar to Teflon, to which sulphonic acid groups are fixed to the polymer and cannot leak out, but the protons of these groups are free to migrate through the membrane.

**Electrodes:-**Typical gas diffusion electrodes, made up of porous C impregnated with Pt catalyst. Noble metal treated carbon fiber paper/cloth which is directly bonded to the polymer membrane at an elevated temperature and pressure (The catalytic electrode/membrane configuration is referred to as membrane electrodes assemble, MEA).

**Fuel:-** Hydrogen

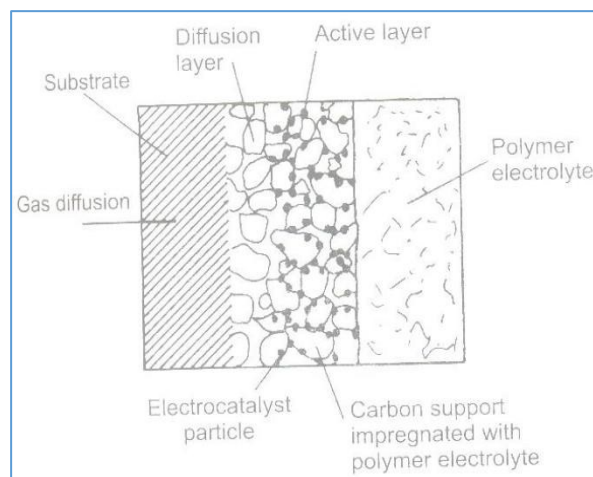
**Oxidant:-** Air

**Catalyst:-**Platinum

**Interconnect:-** Carbon or metal

**Operating temperature:-** 40 – 80 °C.

**Charge-carrier:-** $H^+$



Schematic of a typical PEMFC electrode, which displays three layers

(i) A Teflonized substrate (typically, carbon cloth)

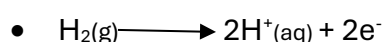
(ii) A diffusion layer, generally formed by carbon particles of about 0.1  $\mu m$  size with Teflon.

(iii) An active layer, where Pt catalyst grains are supported on carbon particles (Pt loading is usually 0.4 mg/cm<sup>2</sup> or less) with or without Teflon.

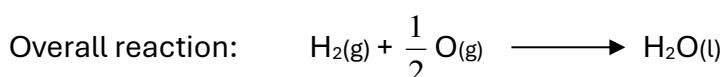
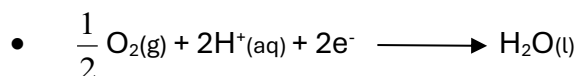
### **Cell reactions and Function of PEMFC:**

PEM fuel cells operate at around 80 °C and practical efficiency of 60 %. Power output is in the range of 5-200 KW. They are ideal for transportation and portable power. Additional advantages are their high response, small size and low cost. A polymer electrolyte membrane fuel cell is unusual in that its electrolyte consists of a layer of solid polymer which allows protons to be transmitted from one fact to the other. Porous carbon is used as the anode and cathode of the PEMFC, as shown in Fig. It basically requires H<sub>2</sub> and O<sub>2</sub> as its inputs, though the oxidant may also be ambient air, and these gases must be humidified. It operates at a low temperature because of the limitations imposed by the thermal properties of the membrane itself. The operating temperatures are around 90°C and a Pt catalyst is used.

At anode:



At cathode



### **Applications:**

- PEM fuel cells are used primarily for transportation applications and some stationary applications.

- Due to their fast startup time, low sensitivity to orientation, and favorable power-to-weight ratio, PEM fuel cells are particularly suitable for use in passenger vehicles, such as cars and buses.

**Advantages:**

- The PEMFC has a solid electrolyte which provides excellent resistance to gas crossover.
- The PEMFCs low operating temperature allows rapid start-up and, with the absence of corrosive cell constituents, the use of the exotic materials required in other fuel cell types, both in stack construction.
- PEMFCs are capable of high current densities of over 2 kW/l and 2 W/cm<sup>2</sup>.

**Disadvantages:**

- The low and narrow operating temperature range makes thermal management difficult, especially at very high current densities, and makes it difficult to use the rejected heat for cogeneration.
- Optimized proton and water transport properties of the membrane and proper water management are crucial for efficient fuel cell operation. Dehydration of the membrane reduces the proton conductivity and excess water can lead to the flooding of the electrolyte. Both the conditions lead to poor performance.
- Perfluorinated membranes have a high cost.
- PEMFCs are quite sensitive to poisoning by trace levels of contaminants including CO, sulfur species and ammonia.

**Differences between the fuel cell and galvanic cell:**

Fuel Cell	Galvanic Cell

1. They do not store chemical energy	They store chemical energy
2. Reactants are fed from outside the cell continuously	The reactants from an integral part of its construction.
3. Need expensive noble metal catalysts & an optimum to an operative for their efficient functioning.	These special conditions are not required
4. Do not get discharged and no need of charging	Get-discharged when stored – up energy is exhausted.
5. Such cells never become dead as long as fresh reactants are available	Limited life span in use
6. Useful for long-term electricity generation.	Useful as portable power services.
7. Reaction products must be continuously removed	No such problem
8. No pollutants are generated (significant environmental benefits)	Pollutants are generated after their useful life
9. Produce power from fuels	They cannot generate electricity from fuels
10. Significantly higher power densities	Lower power density

### **SAFETY CONCERNS WITH LITHIUM-ION BATTERIES**

Lithium-ion batteries are widely used in current electronics because they have a high energy density and can be recharged. Nevertheless, they also pose safety risks, mainly associated with the possibility of thermal runaway, which can result in fires and explosions. Below are many critical safety considerations related to lithium-ion batteries.:

- a. Internal Shorts and Thermal Runaway:** When a lithium-ion battery cell is damaged or malfunctioning, it can experience internal shorts, resulting in fast heating and a chain reaction called thermal runaway. Thermal runaway can cause the electrolyte in the battery to deteriorate and emit flammable gasses, resulting in an accumulation of pressure within the cell. In severe instances, this can result in the battery releasing gas, igniting, or detonating.

- b. Overcharging and Overheating:** Excessive charging of a lithium-ion battery can result in the accumulation of excessive heat, which can then lead to thermal runaway. The majority of lithium-ion batteries are equipped with integrated protective circuits to safeguard against overcharging. However, these circuits can malfunction under specific circumstances. In addition, being exposed to elevated temperatures, such as leaving a gadget inside a hot vehicle, can potentially lead to overheating and thermal runaway.
- c. Physical Damage:** Mishandling a lithium-ion battery by dropping or crushing it can cause harm to the internal components, resulting in short circuits and thermal runaway. It is imperative to use caution while handling lithium-ion batteries and refrain from exposing them to physical impact.
- d. Manufacturing Defects:** Inadequate manufacturing processes or flaws in battery cells might heighten the probability of thermal runaway. Implementing quality control procedures is essential for guaranteeing the safety and dependability of lithium-ion batteries.
- e. Puncture or Penetration:** Intentionally or accidentally puncturing or piercing a lithium-ion battery can result in internal shorts and initiate thermal runaway. Therefore, it is imperative to exercise great care while dealing with defective batteries and ensure their correct disposal.
- f. Age and Degradation:** Over a period of time, lithium-ion batteries undergo degradation, resulting in a decrease in their capacity and performance. As batteries deteriorate over time, they may become increasingly susceptible to overheating and thermal runaway. Adhering to proper maintenance practices, such as preventing severe discharges and exposure to harsh temperatures, may significantly extend the lifespan of lithium-ion batteries.

To reduce the safety hazards linked to lithium-ion batteries, manufacturers incorporate a range of safety measures and practices, including as:

- a. Battery Management Systems (BMS):** The Battery Management System (BMS) oversees and regulates the process of charging and discharging lithium-ion batteries in order to avoid excessive charging, excessive discharging, and overheating.



- b. Thermal Management Systems:** Thermal management devices, such as heat sinks and cooling fans, are used to disperse the heat produced during the process of charging and discharging to prevent thermal runaway.
- c. Quality Control and Testing:** Manufacturers do thorough testing and quality control inspections to detect and rectify possible flaws in battery cells before their release into the market.
- d. Safety Standards and Regulations:** Governments and standards organizations set safety rules and regulations for lithium-ion batteries to guarantee their secure design, production, and utilization.

## ENVIRONMENTAL IMPACT OF BATTERY PRODUCTION

The environmental consequences of battery manufacture differ based on several elements, such as the battery type, the materials employed in its fabrication, the energy sources utilized in the production process, and the existing recycling infrastructure. Below are a few crucial factors to consider about the environmental consequences of battery manufacturing:

- a. Resource Extraction:** The extraction of primary resources for batteries, such as lithium, cobalt, nickel, and graphite, can cause substantial ecological repercussions. Mining activities can result in the degradation of habitats, pollution of soil and water, loss of forests, and the relocation of indigenous tribes. Efforts to mitigate the environmental consequences of resource extraction involve the use of responsible mining techniques and the encouragement of material recycling and reuse.
- b. Energy Intensity:** The processes involved in producing batteries are frequently characterized by high energy consumption, especially during the fabrication of electrode materials and the construction of battery cells. The environmental ramifications of battery manufacture are determined by the energy sources employed in the manufacturing process. Utilizing fossil fuels in the industrial process can lead to the release of greenhouse gases and the generation of air pollution. Adopting renewable energy sources, such as solar or wind power, can decrease the environmental impact of battery manufacturing by reducing carbon emissions.

- c. Chemical Pollution:** The process of battery manufacture necessitates the utilization of many chemicals, a few of which possess the potential to be detrimental to both human health and the environment if not handled with appropriate care. For instance, the manufacturing process of lithium-ion batteries necessitates the use of solvents, electrolytes, and coatings, which could include hazardous compounds. Strict rules and strict adherence to industry standards are crucial to reduce chemical contamination and guarantee the safe handling and disposal of dangerous substances.
- d. Water Usage:** Battery production procedures may need substantial water consumption for purposes such as cooling, cleaning, and chemical processing. The strain on water supplies and the impact on ecosystems might vary depending on the area and the availability of local water. By implementing water conservation measures and practicing water recycling wherever feasible, we may effectively reduce the negative effects caused by water scarcity.
- e. End-of-Life Management:** Efficiently managing the disposal of batteries at the end of their life cycle is crucial to minimize any negative effects on the environment. Improper disposal or lack of recycling of batteries can result in the release of harmful chemicals into the land and water, causing pollution and harm to ecosystems. Developing effective recycling infrastructure and advocating for the reuse of battery materials can contribute to minimizing the environmental impact of battery manufacturing and disposal.

In summary, batteries are vital for facilitating the shift towards renewable energy and electrification. However, it is imperative to carefully assess and mitigate their environmental consequences at every stage of their existence, ranging from the extraction of raw materials to their disposal at the end of their lifespan. Implementing sustainable practices, adopting technical advancements, and establishing regulatory frameworks are essential for addressing the environmental concerns linked to battery manufacture.

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