Battery Technology and Fuel Cells

Galvanic Cell: An electrochemical cell that converts chemical energy of a spontaneous redox reactions into electrical energy.

A Daniel cell is the best example of a galvanic cell which converts chemical energy into electrical energy. It consists of two electrodes of dissimilar metals, Zn and Cu; each electrode is in contact with a solution of its own ion; Zinc sulphate and copper sulphate respectively.It is designed to make use of the spontaneous redox reaction between zinc and cupric ion to produce an electric current.

Daniel Cell

Cell Reactions

Ion Zn/$ZnSO_4$ half cell, oxidation reaction occurs.

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

Ion Cu/CuSO4 half cell, reduction reaction occurs.

$Cu^{2+} + 2e^{-} \rightarrow Cu$

The net cell reaction is

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Cell is represented as

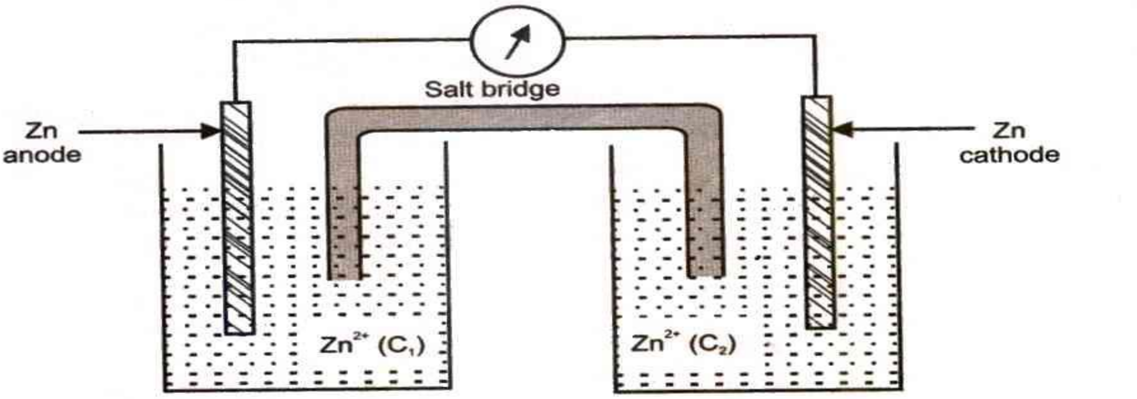
$Zn(s) \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu(S)$

EMF of a cell: The driving force which operates between the two electrodes (cathode and anode) due to the difference in electrode potentials is EMF of the cell or cell potential.

Concentration Cell: A cell containing two electrodes of the same metal dipped in the solution of same electrolyte but of different concentrations.

Eg: A cell in which the electrodes are made up of zinc metal dipped in $ZnSO_4$ solutions of different concentrations C_1 and C_2. The cell is represented as:

$Zn / Zn^{2+} (C_1) // Zn^{2+} (C_2) / Zn$



Numerical problems on Concentration Cells

1.The concentration cell $Ag/AgNO_3$ (0.05M)// $AgNO_3$ (1M)/Ag was constructed by immersing two silver electrodes in $AgNO_3$ solution. Write the cell reaction and calculate the EMF at 25^0C.

Cell Reactions:

Anode Reaction: $Ag \text{ -------}\rightarrow Ag^+ (0.05M) + e^-$

Cathode Reaction: $Ag^+ (1M) + e^- \text{ --------}\rightarrow Ag$

Net cell reaction: $Ag^+ (1\ M) \text{ -------}\rightarrow Ag^+ (0.05M)$

EMF of concentration cell can be given as $E_{Cell} = \frac{2.303RT}{nF} \log \frac{C2}{C1}$

At 25^0C $\quad E_{Cell} = \frac{0.0591}{n} \log \frac{C2}{C1}$

$E_{Cell} = \frac{0.0591}{} \log \frac{1}{0.05}$

$E_{Cell} =$ **0.0768 M**

2.The cell potential of Cu concentration cell Cu **I** Cu^{2+}(0.0093 M) **II** CuSO4(X) **I** Cu is 0.086 V at 25°C. Write cell reactions and calculate the value of X.

Cell Reactions

Anode Reaction: Cu -------→ Cu^{2+} (0.0093M) + 2e-

Cathode Reaction: Cu^{2+} (X M) + 2e- --------→ Cu

Net cell reaction: Cu^{2+} (X M) -------→ Cu^{2+} (0.0093M)

EMF of concentration cell can be given as $E_{Cell} = \frac{2.303RT}{nF} \log \frac{C2}{C1}$

At 25^0C $\qquad E_{Cell} = \frac{0.0591}{n} \log \frac{C2}{C1}$

$$0.086 = \frac{0.0591}{2} \log \frac{X}{0.0093}$$

$$\log \frac{X}{0.0093} = \frac{0.086 X 2}{0.0591}$$

$$= 2.9103$$

$$\frac{X}{0.0093} = \text{antilog } (2.9103) \text{ [i.e } 10^{(2.9103)}]$$

$$= 812.830$$

$$X = 812.830 X 0.0093$$

=**7.55 M**

3. Two cadmium rods immersed in Cadmium Sulphate solution of concentration 0.002 M and 0.4 M. Write the cell representation, cell reaction and calculate the EMF at 25^0C.

Cell Representation: Cd **I** $CdSO_{4\,(0.002M)}$ **II** $CdSO_{4\,(0.4M)}$ **I** Cd

Cell Reactions:

Anode Reaction: Cd -------→ Cd^{2+} (0.002M) + 2e-

Cathode Reaction: Cd^{2+} (0.4 M) + 2e- --------→ Cd

Net cell reaction: Cd^{2+} (0.4 M) -------→ Cd^{2+} (0.002M)

EMF of concentration cell can be given as $E_{Cell} = \frac{2.303RT}{nF} \log \frac{C2}{C1}$

At 25^0C $\quad E_{Cell} = \frac{0.0591}{n} \log \frac{C2}{C1}$

$E_{Cell} = \frac{0.0591}{2} \log \frac{0.4}{0.002}$

E_{Cell} = 0.0291 X 2.3010

= **0.066 M**

4. The cell potential of Cd concentration cell Cd **I** Cd2+(XM) **II** CdSO4(0.025 M) **I** Cd is 0.035 V at 25^0C. Calculate the value of X.

EMF of concentration cell can be given as $E_{Cell} = \frac{2.303RT}{nF} \log \frac{C2}{C1}$

At 25^0C $\quad E_{Cell} = \frac{0.0591}{n} \log \frac{C2}{C1}$

$0.035 = \frac{0.0591}{2} \log \frac{0.025}{X}$

X= **0.0016** M

5.The spontaneous galvanic cell Tin **I** Tin ion (0.02M) **II** Tin ion **(**0.06 M) **I** Tin develops an emf 0.0141 V at 298K. Calculate the valency of tin.

$E_{Cell} = \frac{2.303RT}{nF} \log \frac{C2}{C1}$

At 298 K $\quad E_{Cell} = \frac{0.0591}{n} \log \frac{C2}{C1}$

$n = \frac{0.0591}{ECell} \log \frac{C2}{C1}$

$= \frac{0.0591}{0.0141} \log \frac{0.06}{0.02}$

= **2**

<u>Classification of Batteries :</u>

(1) <u>Primary Batteries :</u>

A primary cell is one in which electrical energy can be obtained at the expense of chemical energy only as long as the active materials are still present. Once these have been consumed, the cell cannot be profitably or readily recharged and must be discarded. Eg.: Dry cell, HgO – Zn cell, Ag_2O – Zinc cell

(2) <u>Secondary cells: (Storage cells)</u>

A secondary cell, once used can be recharged by passing current through it. It can be used over and over again. The redox reaction gets reversed during recharging. The electrical energy is stored in the form of chemical energy and utilized for supplying the current when needed. Secondary cells are also known as storage cells.

Primary cell acts as only galvanic cell. But secondary cell acts both as galvanic cell and electrolytic cell. During discharging it acts as a galvanic cell (C.E. to E.E.) while recharging Electrolytic cell (E.E. to C.E.) E.g.: Lead storage battery, Li-ion battery etc

A lead acid battery is a rechargeable battery that uses lead and sulphuric acid to function. The lead is submerged into the sulphuric acid to allow a controlled chemical reaction. This chemical reaction is what causes the battery to produce electricity.

(3) Reserve Batteries :

The batteries which may be stored in an inactive state and made ready for use by activating them prior to the application are referred to as the reserve batteries. In this type, a key component is separated from the rest of the battery prior to activation. Usually the electrolyte is the component that is isolated. Batteries, which use highly active component material, are designed in this form to withstand deterioration in storage and to eliminate self-discharge prior to use. The reserve design is also used for batteries required to meet extremely long or environmentally severe storage requirements.

In most of the batteries the key component separated from the battery is the electrolyte, thus preventing the chemical reaction in the battery. In lead storage battery by adding 5M H_2SO_4 acid, it can be charged. There are some commercial batteries, which can be activated by adding water or allowing air to enter. E.g.: Mg – H_2O activated batteries

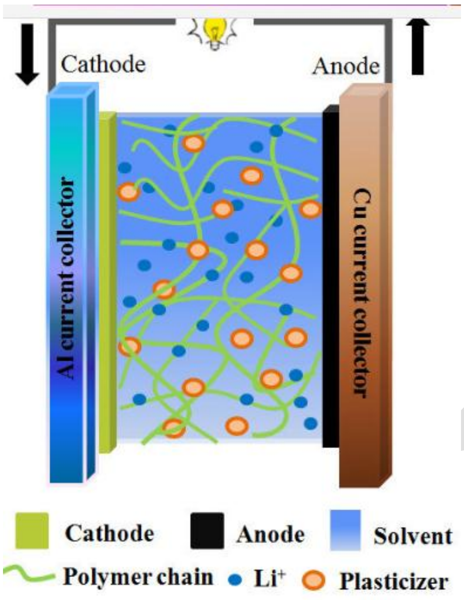
Zn - Ag_2O reserve batteries etc.

Lithium-polymer battery: Lithium-polymer is the most popular rechargeable battery. Lithium-polymer batteries power the devices we use every day, like our mobile phones and electric vehicles.

Principle:

During the discharge of battery the anode releases lithium ions to the cathode, generating a flow of electrons from one side to the other. Opposite process takes place during charging of battery where lithium ions are released by the cathode and received by the anode.

Construction and working



Li- Polymer Battery

Anode: Lithium intercalated Carbon or graphite, metal matrix composite or polymer.(Li_xC_6)

Anode current collector: Copper foil.

Cathode: Partially Lithiated transition metal oxides of nickel, cobalt, and manganese: Li_yNiO_2, Li_yCoO_2 & $Li_yMn_2O_4$.

Cathode current collector: Aluminium foil.

Electrolyte: The battery uses a solid polymer electrolyte (SPE) such as poly(ethylene oxide) (PEO),

The cell reaction during discharge or charging are:

$$\text{At anode: } Li_xC_6 \rightleftarrows xLi^+ + xe^- + 6C$$

$$\text{At cathode: } Li_{1-x}CoO_2 + xLi^+ + xe^- \rightleftarrows LiCoO_2$$

$$\text{Overall reaction: } Li_xC_6 + Li_{1-x}CoO_2 \rightleftarrows LiCoO_2 + 6C$$

The voltage of a single Li-Polymer cell depends on its chemistry and varies from about 4.2 V (fully charged) to about 2.7–3.0 V (fully discharged)

Applications:

a. electric-powered vehicles
b. Grid application
c. Cell phones
d. Drones, radio controlled equipment and aircraft.
e. Personal electronics.
f. Uninterruptible power supply systems.

Na-ion Battery

The **sodium-ion battery** is a type of rechargeable battery that uses sodium ions (Na^+) as its charge carriers. Sodium-ion batteries have a similar design to their lithium-ion counterparts.

Principle:

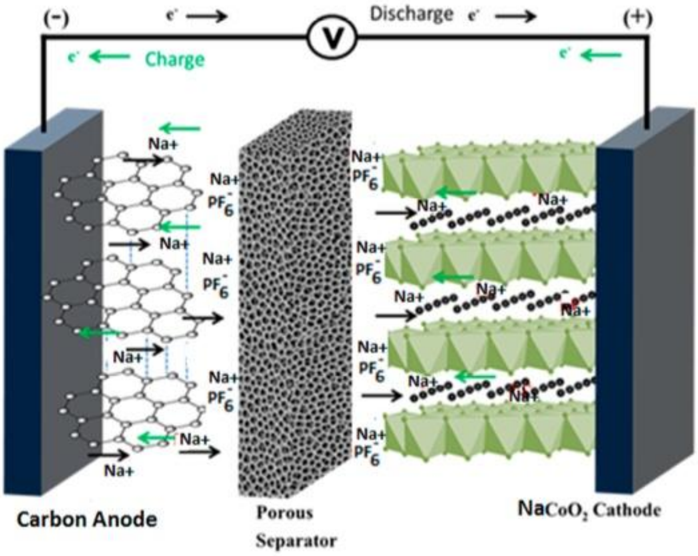
Na-ion battery uses the embedding and stripping process of sodium-ion between positive and negative electrodes for charging/discharging. Na^+ is separated from the positive material and embedded into the negative material through the electrolyte during charging. Electrons are transferred to the negative through the external circuit to maintain charge balance. On the contrary, $Na^+$is removed from the negative electrode and embedded into the positive electrode through an electrolyte.

Construction and Working:

The components of Na-ion batteries are-

Anode materials (negative electrode): carbon-based (hard-carbon), transition metals, and their alloy compounds.

(a) Cathode materials (positive electrode): Metal oxides, Layered oxides, Polyanion phosphate compounds
(b) Electrolyte: Sodium-Ion aqueous electrolyte, Sodium-ion solid polymer electrolyte, Ion electrolyte of SIB



The electrode reactions in a Na-ion battery utilizing hard-carbon (C_6) anode and a layered transition metal oxide, $NaMO_2$, cathode.

The reactions taking place are as follows

At Anode: $\mathbf{Na_xC_6 \rightleftarrows xNa^+ + xe^- + 6C}$

At Cathode: $\mathbf{Na_{1-x}CoO_2 + xNa^+ + xe^- \rightleftarrows NaCoO_2}$

Overall Reaction: $\mathbf{Na_xC_6 + Na_{1-x}CoO_2 \rightleftarrows NaCoO_2 + 6C}$

Applications:

a. Power backup: Data and telecom sectors heavily rely on battery powered infrastructures and operations to drive to the global economy. Na-ion batteries can provide on demand power to ensure safe and seamless power supply.
b. Automobiles and Transportation: In electric vehicles including electric cars and buses.
c. Grid-level applications: Na-ion batteries can help optimise the solar and wind energy to meet grid energy storage requirements.
d. Industrial mobility: Na-ion batteries can maximize asset utilization and minimize operating cost with constant state of readiness and powerful peak power.

Determination of Strength of an acid in Pb-Acid battery.

Principle:

Strength of acid in Lead-Acid battery is a measure of its ability to neutralize the bases to resist change of pH value of acid due to presence of mineral acids like H_2SO_4.

$$H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + H_2O$$

Procedure:

- 50 ml of the acid solution from lead acid battery is taken in 100 ml beaker.
- pH sensor is dipped in it after rinsing with distilled water and connected to the pH meter. The pH of the H_2SO_4 is noted before adding any NaOH to it.
- Now add exactly 0.5ml of NaOH from a semi-micro burette and the solution is stirred well. pH of the resulting solution is noted.
- Addition of each 0.5 ml of NaOH and determination of pH is continued, until a relatively large increase in pH is observed. Now 5 or 6 readings are taken after the equivalence point.
- Plot a graph of Δ pH/ΔV against Vol. of NaOH is plotted and the equivalence point is determined.

Observations and Calculations

Vol. of NaOH in ml.	**pH**	**ΔpH**	**ΔV**	**ΔpH/ΔV**
0				
0.5			0.5	
1.0			0.5	
1.5			0.5	
2.0			**0.5**	
2.5			**0.5**	
3.0			**0.5**	
3.5			**0.5**	
4.0			**0.5**	
4.5			**0.5**	
5.0			**0.5**	
5.5			**0.5**	
6.0			**0.5**	

Normality equation , $N_1V_1 = N_2V_2$

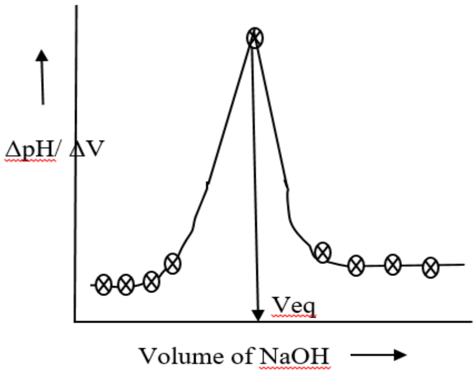
We know that

Normality of NaOH= 0.5N

Volume of sodium hydroxide (V_1) = ……………….ml (from graph)

Volume of Sulphuric acid (V_2) = …………………….ml

Therefore concentration of Sulphuric acid,



$$N_2 = \frac{N_1V_1}{V_2}$$

N_2= ---------------------N

Result: Concentration of acid in Lead-acid battery N_2= ---------------------

Fuel Cells: A fuel cell is an electrochemical cell in which the energy of combustion of a fuel such as hydrogen, methane, carbon monoxide, methanol etc. is derectly converted to electrical energy.

Comparison of fuel cells & a battery.

Fuel cell	Battery
1.Reactants are fed from outside the cell (and not an integral part of the cell)	1. Reactants are an integral part of the battery
2. Chemical energy is not stored in the fuel cell.	2. Chemical energy is stored in the battery.
3. Fuel cells operate as long as reactants are supplied to the electrodes from the outside.	3. Battery operates until the reactants stored i it are completely used up.
4. There is no need to charge a fuel cell.	4. A secondary battery has to be recharged once it is almost used up.
5. Fuel cell has a very high efficiency.	5. Efficiency of a battery is low.

6. Fuel cell has higher energy density.	6. Battery has low energy density.

Advantages of fuel cells:

- Power output is high.
- Do not pollute the atmosphere.
- Electrical energy can be obtained continuously.
- High efficiency.
- Silent operation.
- Nowear &tear.
- Absence of harmful waste products.
- Noneed of charging.

Limitations of fuel cells:

- Cost of power is high as a result of the cost of the electrodes.
- Fuel is in the form of gases and oxygen need to be stored in tanks under high pressure.
- Power output is moderate.
- To have an appreciable voltage, a battery of fuel cells must be available

Types of Fuel Cells

- **Polymer electrolyte membrane fuel cells**: PEFC consists of a gas diffusion layer and an electrode on each side, and a polymer electrolyte membrane in between the electrodes.
- **Direct methanol fuel cells**: A direct methanol fuel cell (DMFC) is an electrochemical energy conversion device that converts the chemical energy of liquid methanol into electrical energy directly.
- **Alkaline fuel cells**: These fuel cells use a solution of potassium hydroxide in water as the electrolyte and can use a variety of non-precious metals as a catalyst at the anode and cathode.
- **Phosphoric acid fuel cells**: Phosphoric acid fuel cells (PAFC) are fuel cells that use liquid phosphoric acid as the electrolyte.
- **Molten carbonate fuel cells**: Molten carbonate fuel cells are high temperature fuel cells, working at 650°C with a molten 62wt% Li2CO3–38wt% K2CO3 eutectic mixture as the electrolyte, CO2 and O2 as oxidant gases and H2 as the fuel.

- **Solid oxide fuel cells**: A solid oxide fuel cell (or SOFC) is an electrochemical conversion device that produces electricity directly from oxidizing a fuel.
- **Reversible fuel cells**: A regenerative fuel cell (RFC), or sometimes called a reversible fuel cell, is a device that can operate alternately as an electrolyzer and as a fuel cell.

Polymer electrolyte fuel cell:

Proton-exchange membrane fuel cells (PEMFC) developed mainly for transport applications, as well as for stationary fuel-cell applications and portable fuel-cell applications. Their distinguishing features include lower temperature/pressure ranges (50 to 100 °C) and a special proton-conducting polymer electrolyte membrane

Principle:

Polymer electrolyte membrane (PEM) fuel cells, also called proton exchange membrane fuel cells, use a proton-conducting polymer membrane as the electrolyte. Hydrogen is typically used as the fuel. These cells operate at relatively low temperatures and can quickly vary their output to meet shifting power demands.

Construction and Working

Anode and Cathode: Porous carbon electrodes impregnated with Platinum.
Electrolyte: Solid polymer membranes capable of H^+ migration used. Teflon-based ion-exchanger membranes containing sulphonic acid group ($-SO_3H$) are frequently used.

H_2 and O_2 are normally used as fuel and oxidant, respectively.

The cell reactions are

At the anode (oxidation):

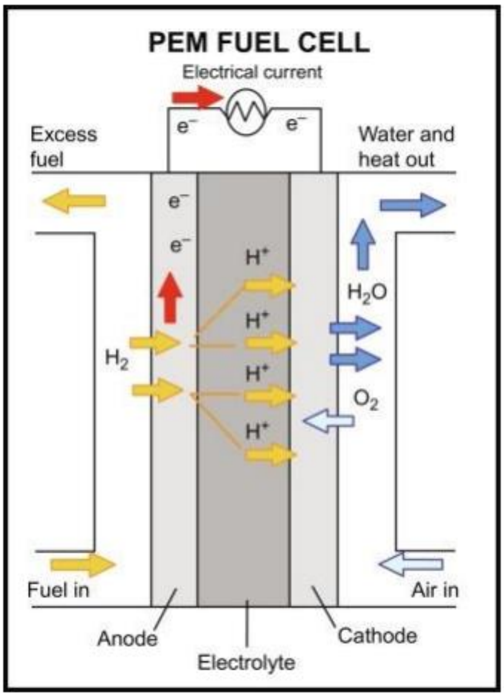
$H_2 \rightarrow 2H^+ + 2e^-$

At the cathode (reduction):

$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

The overall cell reaction:

$H_2 + 1/2O_2 \rightarrow H_2O$



The membranes used to

(a) Provide ionic migration

(b) Separate anodic and the cathodic compartment so that it avoids mixing up of respective species.

The advantage of PEFC is its

- Flexibility in input fuel,
- fast startup,
- Compact design,
- Lightweight,
- Low cost, and solidity of electrolyte.
- It can take pure hydrogen, methanol, as well as formic acid as input.

Applications:

- distributed/stationary and portable power generation.
- Terrestrial transportation applications
- Powering automobiles