Energy Storing Devices

INTRODUCTION

In electrochemical cells, the chemical energy is converted into electrical energy. The cell potential is related to free energy change (ΔG). In an electrochemical cell, the system does work by transferring electrical energy through an electric circuit. Thus □G for a reaction is a measure of the maximum useful work, that can be obtained from a chemical reaction.

i.e., ΔG = maximum work

But we know that

maximum work = nFE

When a cell operates, work is done on the surroundings (flow of electricity).

ΔG = –nFE (or) □$\Delta G < 0$

Decrease in free energy is indicated by (–)ve sign.

One of the main uses of the galvanic cells is the generation of portable electrical energy. These cells are known as batteries.

Definition

A battery is an arrangement of several electrochemical cells connected in series, that can be used as a source of direct electric current.

Thus,

A cell : Contains only one anode and cathode.

A Battery : Contains several anodes and cathodes.

Requirements of a battery

A useful battery should fulfill the following requirements.

1. It should be light and compact for easy transport.
2. It should have long life both when it is being used and when it is not used.
3. The voltage of the battery should not vary appreciably during its use.

TYPES OF BATTERY

1. **Primary Battery (or) Primary cells**

   In these cells, the electrode and the electrode reactions cannot be reserved by passing an external electrical energy. The reactions occur only once and after use they become dead. Therefore, they are **not chargeable.**

   Example : Dry cell, mercury cell.
2. **Secondary Battery (or) Secondary cells**

   In these cells, the electrode reactions can be reversed by passing an external electrical energy. Therefore, they can be recharged by passing electric current and used again and again. These are also called **Storage cells** (or) **Accumulators.**

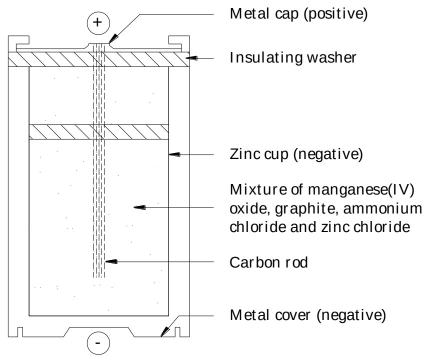
   Example : Lead acid storage cell, Nickel - cadmium cell.
3. **Flow battery (or) Fuel cell**

In these cells, the reactants, products and electrolytes are continuously passing through the cell. In this chemical energy gets converted into electrical energy.
Example : Hydrogen - oxygen fuel cell.

IMPORTANT PRIMARY BATTERIES DRY CELL OR LECLANCHE'S CELL

Description

A dry cell consists of a Zinc cylinder, which acts as anode. This zinc cylinder is filled with an electrolyte consisting of NH_4Cl, $ZnCl_2$ and MnO_2 in the form of paste using starch and water. A carbon rod(graphite), acts as cathode, is immersed in the electrolyte in the centre of the cell. The zinc cylinder has an outer insulation of cardboard case. During use, the zinc cylinder gets consumed and at the end, it will develop holes which are responsible for leakage.



Leclanche's cell

Working

When the cell is working, zinc loses electrons and Zn^{2+} ions gets dissolved in the electrolyte. The electrons pass through the circuit and are consumed at cathode. This causes discharge of ions from the electrolyte.

Cell reactions :

At anode : $Zn \rightarrow Zn^{2+} + 2e^-$

At cathode : $NH_{4(aq)}^{+} + MnO_{2(s)} + 2e^- \rightarrow MnO(OH^-) + NH_3$

Overall Reaction : $Zn + NH_{4(aq)}^{+} + MnO_{2(s)} \rightarrow Zn^{2+}\ MnO(OH)^- + NH_3$

In cathode reaction, Mn is reduced from +4 oxidation state to +3 oxidation state. The liberation of NH3 gas, which disrupts the current flow, is prevented by a reaction of $NH_{3(g)}$ with Zn^{2+} (from $ZnCl_2$).

$$ZnCl_2 + 2NH_3 \rightarrow [Zn(NH_3)_2]\,Cl_{2(s)}$$

The voltage of Leclanche's cell is about 1.5V.

Examples for drycell : Silver cell, Lithium cell.

Disadvantages

1. This dry cell does not have an indefinite life, because NH_4Cl being acidic corrodes the zinc container, even if it is not used.
2. When current is drawn rapidly from it, products build up on the electrodes, so voltage drop occurs.

Uses

It is used in transistor radios, calculators, Flash lights, torches etc.,

MERCURY CELL

It is a small form of dry cell, used in watches, hearing aids.

Uses

It consists of a zinc anode and a mercury (II) oxide cathode. The electrolyte is a paste of KOH and ZnO.

Cell reactions :

At anode :

$$Zn + 2OH^- \rightarrow ZnO_{(s)} + H_2O + 2e^-$$

At cathode :

$$HgO_{(s)} + H_2O + 2e^- \rightarrow Hg_{(1)} + 2OH^-$$

Overall Reaction :

$$Zn + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(1)}$$

Since the overall reaction does not involve any ion in solution, it has the advantage that its potential remains almost constant throughout its life.

The voltage of mercury cell is about 1.35 V.

ALKALINE BATTERY

Description

It is an improved form of the drycell, in which the electrlyte NH_4Cl is replaced by KOH. In alkaline battery, the powdered zinc is mixed with KOH & MnO_2 to get a gel. A carbon rod (grpahite), acts as cathode, is immersed in the electrolyte in the centre of the cell. The outside cylinderical Zinc body is made of Zinc.

Cell reactions :

At anode :

$$Zn_{(s)} + 2OH^-{}_{(aq)} \rightarrow Zn(OH)_{2(s)} + 2e^-$$

At cathode :

$$2MnO_{2(s)} + H_2O(I) + 2e^- \rightarrow Mn_2O_{3(s)} + 2OH^-{}_{(aq)}$$

Overall Cell Reaction :

$$Zn_{(s)} + 2MnO_{2(s)} + H_2O_{(I)} \rightarrow Zn(OH)_{2(s)} + Mn_2O_{3(s)}$$

Advantages of alkaline battery over dry Battery

The main advantages of alkaline battery overy dry battery are

i) Zinc does not dissolve readily in a basic medium.

ii) The life of alkaline battery is longer than the dry battery, because there is no corrosion on Zn.

iii) Alkaline battery maintains its voltage, as the current is drawn from it.

Uses

It is used in calculators, watches etc.,

IMPORTANT SECONDARY BATTERIES

LEAD STORAGE CELL OR LEAD ACCUMULATOR OR ACID STORAGE CELL

Storage Cell

A storage cell is the one, which can operate both as a voltaic cell and as an electrolytic cell. When it acts as a voltaic cell, it supplies electrical energy and becomes “run down”. When it is recharged, the cell operates as an electrolytic cell.

Description

A lead - acid storage battery consists of a number of (3 to 6) voltaic cells connected in series to get 6 to 12 V battery. In each cell, the anode is made of lead. The cathode is made of lead dioxide PbO_2 or a grid made of lead, packed with PbO_2. A number of lead plates (anodes) are connected in parallel and a number of PbO_2 plates (cathodes) are also connected in parallel. Various plates are separated from the adjacent ones by insulators like rubber or glass fibre. The entire combinations is then immersed in dil. H_2SO_4 (38% by mass) having a density of 1.30 gm/ml.

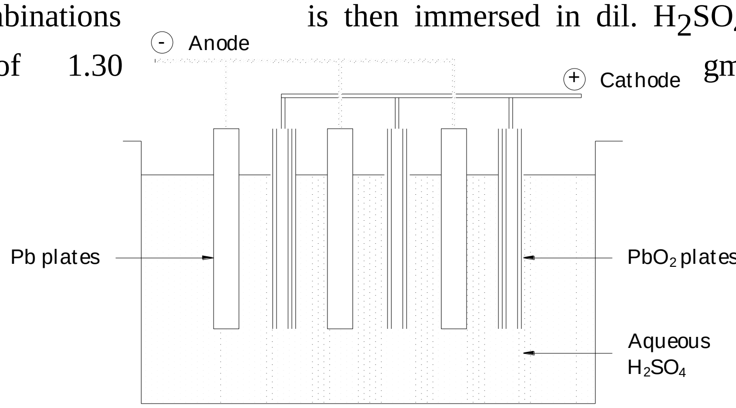


Fig. 5.2 Lead storage cell

The cell may be represented as;

$$Pb / PbSO_4 // H_2SO_{4(aq)} / PbO_2 / Pb$$

Working (Discharging)

When the lead - acid storage battery operates, at the anode lead is oxidised to Pb^{2+} ions and insoluble $PbSO_4$ is formed. At the cathode PbO_2 is reduced to Pb^{2+} ions and $PbSO_4$ is formed.

Cell reactions :

At anode : Lead is oxidised to Pb^{2+} ions, which further combines with forms insoluble $PbSO_4$.

$$Pb_{(s)} \rightarrow Pb^{2+}{}_{(aq)} + 2e^-$$

$$Pb^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)}$$

Overall anode Reaction :

$$Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$$

At cathode :

PbO_2 gains electrons ie., Pb undergoes reduction at the cathode from +4 to +2. The Pb^{2+} ions then combines with ions forms insoluble $PbSO_4$.

$$PbO_{2(s)} + 4H^+ + 2e^- \rightarrow Pb^{2+}{}_{(aq)} + 2H_2O$$

$$Pb^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)}$$

Overall Cathode Reaction

$$PbO_{2(s)} + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$$

Overall cell reaction during use (discharging)

At anode : $$Pb_{(s)} + SO_4^{2-}{}_{(aq)} \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} 2PbSO_{4(s)} + 2e^-$$

At cathode : $$PbO_{2(s)} + 4H^+ + SO_4^{2-} + 2e^- \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} PbSO_{4(s)} + 2H_2O$$

Overall cell reaction :

$$Pb_{(s)} + PhO_{2(s)} + 2H_2SO_{4(aq)} \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} 2PbSO_{4(s)} + 2H_2O + \text{Energy}$$

From the above cell reaction it is clear that, $PbSO_4$ is precipitated at both the electrodes and H_2SO_4 is used up. As a result, the concentration of H_2SO_4 decreases and hence the density of H_2SO_4 falls below 1.2 gm/ml. So the battery needs recharging.

Recharging the Battery

The cell can be charged by passing electric current in the opposite direction. The electrode reaction gets reversed. As a resulty, Pb is deposited on anode and PbO_2 on the cathode. The density of H_2SO_4 also increases.

The net reaction during charging is

$$2PbSO_{4(s)} + 2H_2O + \text{Energy} \underset{\text{discharging}}{\overset{\text{charging}}{\rightleftharpoons}} Pb_{(s)} + PbO_{2(s)} + 4\,H^+ + 2SO_4^{2-}$$

Uses

1. Lead storage cell is used to supply current mainly in automobile such as cars, buses, trucks, etc.,
2. It is also used in gas engine ignition, telephone exchanges, hospitals, power stations etc.,

NICKEL - CADMIUM CELL

This is also a rechargeable battery.

Description

Nickel - cadmium cell consists of a cadmium anode and a metal grid containing a paste of NiO_2 acting as a cathode. The electrolyte in this cell is KOH.

It is represented as : $Cd / Cd(OH)_2 // KOH_{(aq)} / NiO_2 / Ni$

Working (Discharging)

When the Nicad battery operates, at the anode cadmium is oxidised to Cd^{2+} ions and insoluble $Cd(OH)_2$ is formed. It produces about 1.4V.

Cell reactions

At anode : Cadmium is oxidised to Cd^{2+} and further it combines with OH^- ions to form $Cd(OH)_2$.

$$Cd_{(s)} + 2OH^- \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} Cd(OH)_{2(s)} + 2e^-$$

At cathode : NiO_2 gains electrons, i.e., Ni undergoes reduction at the cathode from +4 to +2. The Ni^{2+} ions then combine with OH^- ions to form $Ni(OH)_2$.

$$NiO_{2(s)} + 2H_2O + 2e^- \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} Ni(OH)_{2(s)} + 2OH^-$$

Cell reactions during use (discharge)

At anode :

$$Cd_{(s)} + 2OH^- \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} Cd(OH)_{2(s)} + 2e^-$$

At cathode :

$$NiO_{2(s)} + 2H_2O + 2e^- \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} Ni(OH)_{2(s)} + 2OH^- + Energy$$

Overall cell reaction :

$$Cd_{(s)} + NiO_{2(s)} + 2H_2O \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} Cd(OH)_{2(s)} + Ni(OH)_{2(s)} + \text{Energy}$$

From the above cell reactions it is clear that, there is no formation of gaseous products, the products $Cd(OH)_2$ and $Ni(OH)_2$ adhere well to the surfaces. This can be reconverted by recharging the cell.

Recharging the Battery

The charging process is similar to lead storage battery. When the current is passed in the opposite direction, the electrode reaction gets reversed. As a result, Cd gets deposited on anode and NiO_2 on the cathode.

The net reaction during charging is

$$Cd(OH)_{2(s)} + Ni(OH)_{2(s)} + Energy \underset{\text{discharging}}{\overset{\text{charging}}{\rightleftharpoons}} Cd_{(s)} + NiO_{2(s)} + 2H_2O$$

Advantages

1. It is smaller and lighter.
2. It has longer life than lead storage cell.
3. Like a dry cell, it can be packed in a sealed container.

Disadvantages

It is more expensive than lead storage battery.

Uses

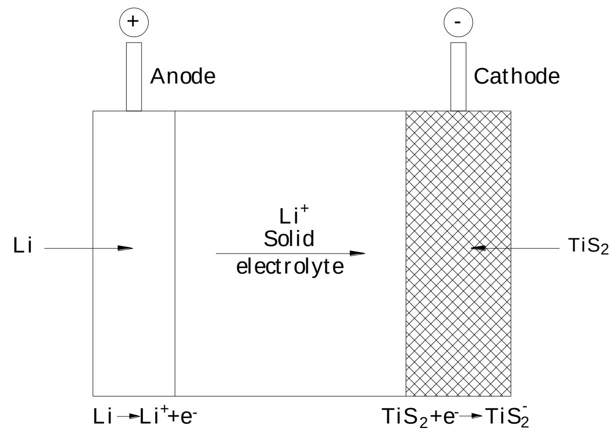
It is used in calculators, electronic flash units, transistors and cordless appliances.

LITHIUM BATTERY

Lithium battery is a solid state battery because instead of liquid or a paste electrolyte, solid electrolyte is used.

Construction:

The lithium battery consists of a lithium anode and a TiS_2 cathode. A solid electrolyte, generally a polymer, is packed in between the electrodes. The electrolyte (polymer) permits the passage of ions but not that of electrons.



Solid state lithium battery

Various reactions

The various electrode reactions are

At anode : $Li(s) \rightarrow Li^{+} + e^{-}$

At cathode : $TiS_{2(s)} + e^{-} \rightarrow TiS_{2}^{-}$

Overall cell reaction :

$$Li(s) + TiS_{2(s)} \rightarrow Li^{+} + TiS_{2}^{-}$$

$$Li^{+} + TiS_{2}^{-} \rightarrow LiTiS_{2}$$

This cell is rechargeable and produces a cell voltage of 3V.

Othertypes of Secondary Lithium Batteries

i) Li / MnO_2
ii) Li / V_2O_5
iii) Li / MoO_2
iv) Li / Cr_3O_8

Advantages of Li battery

It is the cell of future, why?

i) Its cell voltage is high, 3V.
ii) Since Li is a light-weight metal, only 7g (1 mole) material is required to produce 1 mole of electrons.
iii) Since Li has the most negative E^{o} value, it generates a higher voltage than the other types of cells.
iv) Since all the constituents of the battery are solids there is no risk of leakage from the battery.
v) This battery can be made in a variety of sizes and shapes.

Lithium - Sulphur Battery :

Lithium - Sulphur battery is a rechargeable battery. Its anode is made of Li. Sulphur is the electron acceptor, the electron from Li is conducted to S by a graphite cathode. -Alumina ($NaAl_{11}O_{17}$) is used as the solid electrolyte.

This solid electrolyte allows the Li^+ ions to migrate to equalize the charge, but will not allow the big poly sulphide product ions.

This battery is operated at high temperatures as Li and S should be in their molten states.

Various reactions

The various electrode reactions are

At anode : $2Li \rightarrow 2Li^+ + 2e^-$

At cathode : $S + 2e^- \rightarrow S^{2-}$

Overall cell reaction : $2Li + S \rightarrow 2Li^+ + S^{2-}$

The S^{2-} ions, formed, react with elemental sulphur to form the polysulphide ion.

$$S^{2-} + nS \rightarrow [S_{n+1}]^{2-}$$

The direct reaction between Li and S is prevented by the alumina present in the cell.

Advantages of Li-S battery

1. Li-S battery has light weight unlike the lead acid battery.
2. It possess a high energy density.
3. It is used in electric cars.

FUEL CELLS

Definition

Fuel cell is a voltaic cell, which converts the chemical energy of the fuels directly into electricity without combustion. It converts the energy of the fuel directly into electricity.In these cells, the reactants, products and electrolytes pass through the cell.

Fuel + Oxygen Oxidation products + Electricity

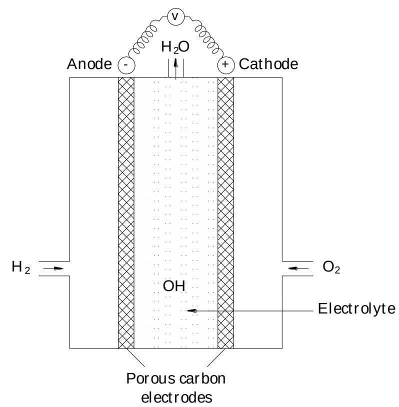
Examples : Hydrogen - oxygen fuel cell; Propane - oxygen fuel cell; Methyl alcohol - oxygen fuel cell.

Hydrogen - Oxygen fuel cell

Hydrogen - oxygen fuel cell is the simplest and most successful fuel cell, in which the fuel - hydrogen and the oxidiser - oxygen and the liquid electrolyte are continuously passed through the cell.

Description

It consists of two porous electrodes anode and cathode. These porous electrodes are made of compressed carbon containing a small amount of catalyst (Pt, Pd, Ag). In between the two electrodes an electrolytic solution such as 25% KOH or NaOH is filled. The two electrodes are connected through the voltmeter.



H_2 - O_2 Fuel cell

Working

Hydrogen (the fuel) is bubbled through the anode compartment, where it is oxidised. The oxygen (oxidiser) is bubbled through the cathode compartment, where it is reduced.

At cathode

The electrons produced at the anode pass through the external wire to the cathode, where it is absorbed by oxygen and water to produce hydroxide ions.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

At anode

Hydrogen molecules are oxidised at the anode with the liberation of electrons, which then combine with hydroxide ions to form water.

$$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$$

Cell reactions

At anode :

$$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$$

At cathode :

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Overall cell reaction :

$$2H_2 + O_2 \rightarrow 2H_2O$$

The emf of the cell = 0.8 to 1.0V

Fuel Battery

When a large number of fuel cells are connected in series, it form fuel battery.

Characteristics (or) advantages

1. **Continuous source of energy :** There is no electrode material to be replaced as in ordinary battery. The fuel is continuously supplied to produce power.
2. **High efficiency :** The fuel cell converts the energy of a fuel directly into the electricity, they are more efficient (70%) than the conventional methods (40%) of generating electricity.
3. **Pollution free working :** There are no objectionable by-products and therefore, they do not cause pollution problems (like noise, vibration, heat transfer, thermal pollution).

Uses

1. H_2 - O_2 fuel cells are used as auxilliary energy source in space vehicles, submarines or other military - vehicles.
2. In case of H_2 - O_2 fuel cells, the product of water is proved to be a valuable source of fresh water by the astronauts.

PHOTOGALVANIC CELL OR SOLAR CELL

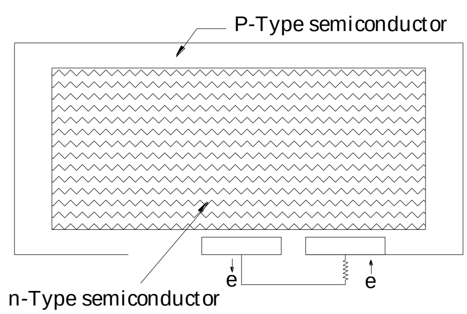
Definition

Photogalvanic cell is the one, which converts the solar energy (energy obtained from the sun) directly into electrical energy.

Solar battery

When a large number of photogalvanic cells are inter connected, forms solar battery.

Description



Solar Cell

Photogalvanic cell consists of a p-type semiconductor (such as Si doped with B) and a n-type semi conductor (such as Si doped with P). They are in close contact with each other, so that a limited extent of electrons (from n-type semiconductor) and positive holes (from-type semiconductor) can cross the junction between the two types of semiconductors.

Working

When the solar rays fall on the outer layer of p-type semiconductor, the electrons in the valence band get promoted to the conduction band by absorbing the light energy. Since the conduction electrons, unlike the positive holes, can easily cross the p-n junction into the n-type semiconductor, a potential difference between two layers is created. This potential difference causes flow of electrons (ie., an electric current). The potential difference and hence current increases as more solar energy falls on the surface of the outer layer. When this p-and n-layers are connected to an external circuit, electrons flow from n-layer to p-layer, there by the current is generated.

QUESTIONS

1. What is Leclanche's cell? How does it work?
2. Write notes on (i) Mercury cell (ii) Alkaline battery.
3. Explain discharging and charging process of lead storage cell.
4. Explain description and working of NICAD battery.
5. Write notes on lithium battery.
6. What are fuel cells? Explain the construction and working of hydrogen - oxygen fuel cell.