Module 5 : Electrochemistry
Lecture 23 : Batteries and Fuel Cells

Objectives

After studying this lecture you will be able to

- Classify electrochemical energy sources into different types.
- Analyze the design and working of primary cells.
- Analyze the design and working of secondary cells.
- Analyze the working of fuel cells.
- Analyze the design and working of photovoltaic solar cells.

23.1 Introduction :

Commercial cells which are used as sources of electrical energy are of three main types: Primary cells, secondary cells and fuel cells. Primary cells are based on cell reactions which are not reversible. Once the cell reaction is complete, the cell is discharged and cannot be recharged again. Examples: Weston Cd Cell, Leclanche' cell (dry cell) etc.

Secondary cells (storage cells or Accumulators) are galvanic cells in which the cell reactions that produce the current can be reversed by applying an external source of current. These can be discharged and recharged many times until the electrode materials last. Examples: Lead-acid battery, Nickel-Cadmium battery, NiFe cells, etc. The term 'battery' is normally used to denote a number of galvanic cells connected in series.

Fuel cells are also galvanic cells in which the reactants, to be oxidised at the anode (fuels) and reduced at the cathode (oxidants), are provided continuously from external sources and the products are removed as they are formed. In a conventional cell, the reactants form a part of the cell. These are not replenished in primary cells but replenished in secondary cells.

23.2 Primary Cells

We will first consider a modified Ledanche's Cells in which an aqueous solution of the electrolyte is mixed with enough flour or starch to prevent spillage of the electrolyte. It can be represented as

$$Zn \overset{-}{|} NH_4Cl\ (\ 25\%\ ) + ZnCl_2\ (\ 10\%) + Mn0_2\ (s) + C\ (s) \overset{+}{|} \text{Graphite}$$

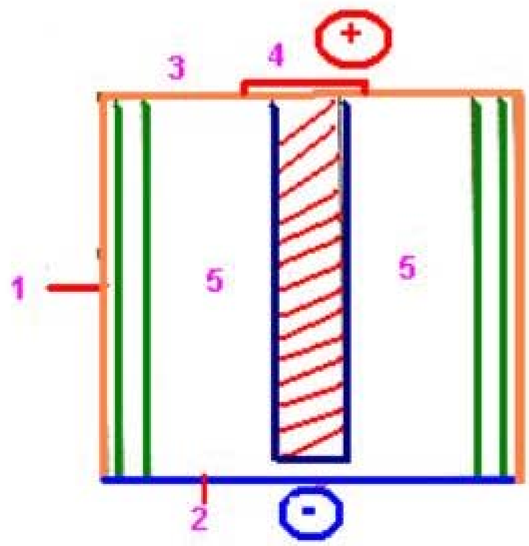

Figure 23.1 : Schematic Representation of a Dry Cell (Primary cell)

1] Outer Cardboard Cover 2]. Zinc Cup anode (Negative Electrode) 3] Plastic or Pitch seal 4] Graphite rod , cathode (positive Electrode) 5. Electrolyte (20 % NH_4 Cl + 10% Zn Cl_2 + $Mn0_2$ (s) + carbon, thickened with starch.

The above dry cell is capable of delivering 1.5 V and the cell reactions can be represented as:

Anode: $Zn - 2e^- = Zn^{2+}$ (oxidation)

Cathode: $2\ MnO_2 + 2\ H_2O + 2\ e^- = 2\ MnO\ (\ OH\ ) + 2\ OH^-$ (reduction)

Cell reaction: $Zn + 2\ MnO_2 + 2\ H_2O = Zn^{2+} + 2\ MnO\ (\ OH) + 2\ OH^-$

MnO_2 is called the 'depolariser', since it prevents the formation of H_2 at the cathode by preferentially getting reduced at the cathode. A secondary reaction (local action) results in the consumption of anode material and the electrolyte during the discharging of the cell. Once discharged, the dry cell cannot be charged for reuse. Dry cells deteriorate on storage due to local action and also due to the evaporation of water from the electrolyte.

$Zn^{2+} + 2OH^- + 2NH_4Cl \longrightarrow Zn\ (NH_3\ )_2Cl_2\ (s) + 2\ H_2O$

A few other common cells will now be outlined.

Miniature flat and round cells, capable of delivering 1.5 V, are used in calculators, hearing aids etc. In the alkaline manganese cell, zinc is the anode, a mixture of MnO_2 and graphite is the cathode and the electrolyte is a solution of KOH contained in an absorbent material. The overall cell reaction is :

$Zn(\ s) + 2MnO_2\ (s) + H_2O \longrightarrow ZnO + H_2O + 2\ MnO\ (OH)$

The silver oxide-Zn cell, though costlier, lasts for a longer time. Here the anode is Zn, cathode is Ag_2O and the electrolyte is the KOH (aq). The cell reaction is:

$Zn + AgO + H_2O \longrightarrow ZnO + H_2O + Ag$

23.3 Secondary Cells

The widely used automobile battery is a storage battery capable of delivering either 6 V or 12 V depending on the number of cells connected in series. These are used as stationary power sources in telephone exchanges, switching systems, emergency lighting etc. The cell can be represented as

$$Pb\ (grid)\ \overset{-}{|}\ PbSO_4\ (s)\ |\ H_2SO_4\ (aq,\ 38\ \%\ by\ weight)\ |\ PbO_2\ (s)\ \overset{+}{|}\ Pb\ (grid)$$

Electrode reactions

Anode:

$Pb\ (s) + SO^{2-}_4 = PbSO_4\ (S) + 2e^-$

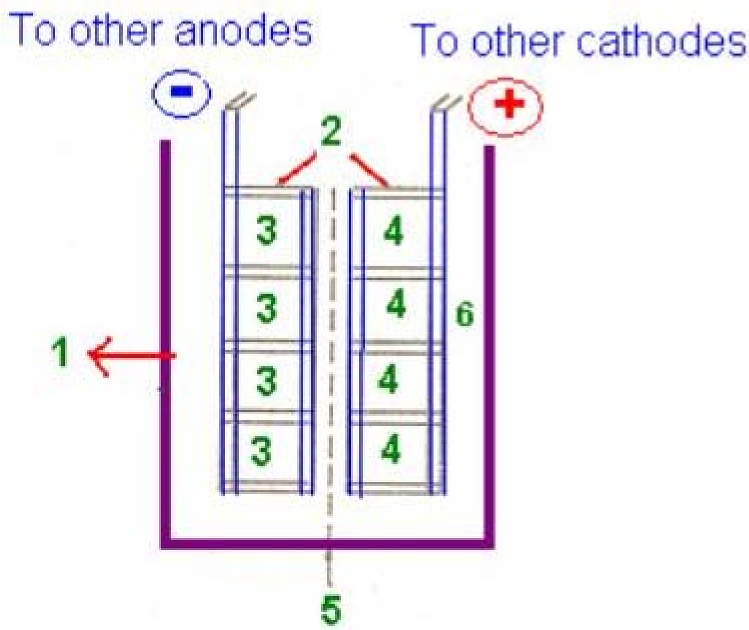

Figure 23.2: Schematic representation of a lead accumulator (Secondary cell)

1. Glass or Plastic container . 2. Grill electrodes made of Pb - Sb alloy. 3. Spongy lead packed in anode.
4. PbO_2 packed in cathode. 5. Porous non-conductive Plastic Separator. 6. Electrolyte (38% by weight of H_2SO_4) sp. gravity = 1.30.

Cathode:

$PbO_2(s) + 4H^+ +$  $+ 2e = PbSO_4\ (s) + 2H_2O$

Cell reaction for the passage of 2F

$$PbO_2 + Pb + 2\,H_2SO_4 \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O \qquad (23.1)$$

The normal voltage of a single lead storage cell is about 2.0 V. As the cell discharges electricity, $PbSO_4$ is deposited on both the electrodes and sulphuric acid is consumed, resulting in a decrease in the specific gravity of the electrolyte. With the aid of a hydrometer, the specific gravity can be checked and if it is equal to or below 1.20 (approx. 28% by weight of H_2SO_4) the battery is (re)charged. The charging operation is performed in such a way that the negative pole of the battery is connected to the negative pole and the positive pole to the positive pole of the external charging device. The charging is done in an automobile by its electrical generator or alternator. During the charging operation, water is converted into sulphuric acid (refer to Eqn.23.1). The charging is done till the specific gravity increases to the required value.

23.4 Nickel-Cadmium Batteries

In these batteries, the electrolyte is 21 % by weight aqueous solution of KOH. The cell can be represented as

$\mathrm{Cd} \overset{-}{|} \mathrm{KOH} \overset{+}{|} \mathrm{NiO(OH)}$

anode .... cathode

$$\mathrm{Cd + 2\,NiO\,(\,OH\,) + 2H_2O \underset{charging}{\overset{discharging}{\rightleftharpoons}} Cd\,(\,OH\,)_2 + 2\,Ni\,(\,OH\,)_2}$$

The voltage of single Ni-Cd cell is 1.3 to 1.4 V. Compared to a lead storage battery, this battery has a longer life. It is also available as a sealed unit for use in electronic flash units (photography) and in calculators.

The search is on for more efficient batteries for the following features:

(i) storing electric power generated during the hours of low consumption, for later use during the periods of peak consumption

(ii) storing electricity form solar and wind-powered generators, and

(iii) use in developing quietly-running, non-polluting electric automobiles and mopeds. Though the lead-acid and the Ni-Cd batteries have been used to replace the internal combustion engines of automobiles, their performance is not as good as the gasoline-powered vehicles. Lithium or sodium-sulphur batteries have been developed for this purpose.

Their drawbacks are:

(a) higher temperatures required for efficient operation,

(b) use of metals capable of violently reacting with water, and

(c) the necessity of using corrosion resistant materials.

23.5 Fuel Cells

Fuel cells convert the energy of combustion directly to electrical energy. A fuel cell can be represented as

Fuel $\overset{-}{|}$ Electrode | Electrolyte | Electrode $\overset{+}{|}$ Oxidant

The common fuels are H_2, N_2H_4 and Hydrocarbons. The major oxidants are Oxidants O_2, H_2O_2, HNO_3, etc

A fuel cell is a galvanic cell in which the chemical energy associated with the oxidation of reducing agents (fuels) is directly converted into electrical energy. The conventional method of utilizing the chemical energy of the fuel to produce electrical energy and the direct conversion process used in the fuel cell can be represented as shown below.

$$\begin{tikzcd} \text{Chemical energy} \arrow[r, "(d)"] \arrow[d, "(a)"'] & \text{Electrical energy} \\ \text{Thermal energy} \arrow[r, "(b)"] & \text{Mechanical energy} \arrow[ul, "(c)"'] \end{tikzcd}$$

Any losses in energy in steps (a) and (c) can be minimized. However the efficiency of the process (b) is limited by the second law of thermodynamics. Hence the process (d) might be expected to have a higher efficiency. If ΔH is the enthalpy change of the reaction, the amount of useful work that can be obtained out of this is ΔG. The rest of it. i.e., $\Delta H - \Delta G = T\,\Delta S$ is unavailable for work.

Efficiency = E = Work obtained from the cell reaction / Heat change accompanying the reactIon = $\Delta G / \Delta H$

$E = \Delta G / \Delta H = 1 - T(\Delta S / \Delta H)$

Thus, E depends on both ΔS and ΔH.

The combustion (oxidation) reaction

$2H_2(g) + O_2(g) = 2H_2O$, can be made to occur in a galvanic cell of the type (Fig. 23.3)

Inert electrode $\overset{-}{|}\ H_2(g) \mid H^+ \mid O_2(g)\ \overset{+}{|}$ Inert electrode

Anode: $2H_2 + 4H_2O = 4H_3O^+ + 4e$ ($E^0 = 0$)

Cathode: $O_2 + 4H_3O^+ + 4e = 6H_2O$ ($E^0 = 1.23$ V)

In the H_2- O_2 fuel cell, the electrodes are Ti coated with porous Pt, and a water-soaked caution exchange resin in the acid form is used as the electrolyte. If the pressure of the gases are 1 atm, and water in the resin is pure, the EMF of this cell should be + 1.23 V, corresponding to the cathode reaction $O_2 + 4H_3O^+ + 4e = 6H_2O$.

This is because the potential of the hydrogen electrode under these conditions is zero. In practice, the emf is about 0.8 to 1.0 V.

The only product discharged by the cell is water. The electrolyte in a H_2 - O_2 fuel cell may also be alkaline.

The electrode reactions in this case are

$O_2 + 2H_2O + 4e^- = 4OH^-$; $E^0 = +0.40$ V

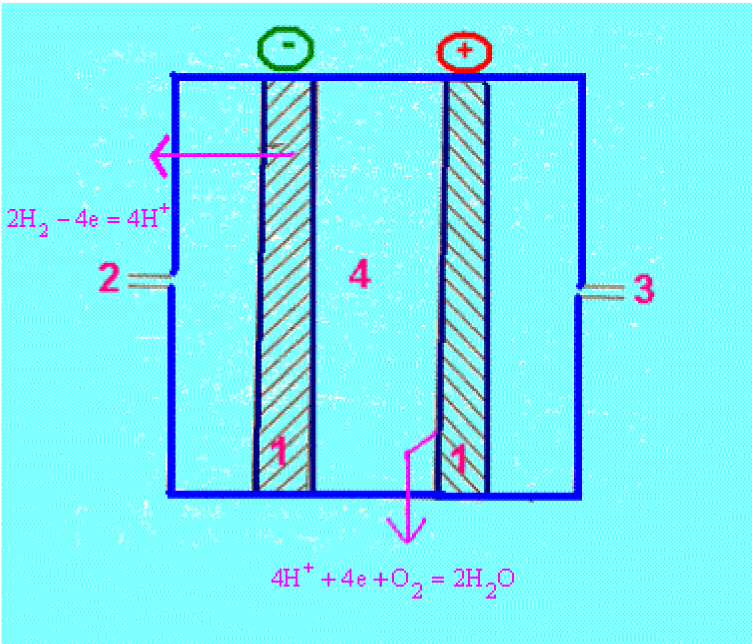

Figure 23.3 : Schematic representation of a H_2 - O_2 fuel cell using H_3O^+ as electrolyte

1] Ti electrodes coated with porous Pt, 2] Fuel (H_2) inlet, 3] Oxidiser (O_2) inlet, 4] Caution exchange membrane in acid form (source of H^+).

Figure 23.4 : Schematic representation of a fuel cell (H_2 - O_2) using an alkaline electrolyte

1. Porous Ni anode, 2] Porous Ni - NiO cathode, 3] H_2 inlet, 4] O_2 inlet, 5] Electrolyte, KOH (aq)

$4\,H_2O + 4e^- = 2H_2 + 4OH^-$; $E^0 = -0.83$ V

$\therefore\ 2H_2 + O_2 = 2H_2O$; $E^0 = +\,1.23$ V

In spite of higher efficiencies, fuel cells are rather expensive because of the difficult reaction conditions and the requirements of specific catalysts and electrodes. However they are used in space-crafts because of their light weight and also because the product of oxidation, water, can be used by astronauts.

23.6 Photovoltaic(PV) Solar Cells

A very important application of light energy for the generation of electrical power comes from the photovoltaic (PV) solar cell. A PV solar cell is made up of n- and p-type materials of either the same or different compounds. For example, photovoltaic solar cells made out of polycrystalline n-Si and p-Si are commercially available. Pure silicon material is made n-type (electron donating) by doping it with phosphorous and p-type by doping it with boron. When n- and p-type Si are joined together, an electric field is developed at their interface due to the difference in the energy of their electrons. This field makes the n-type semiconductor negatively charged while the p-type semiconductor becomes positively charged. When the junction is illuminated with photons of energy greater than the band gap of Si, excited electrons due to the presence of the electrical field are forced towards n-type and holes (generated due to the creation of vacancy in the valence band) are forced to reach the p- type material. As a result of this, both ends of n- and p- type semiconductors become more charged than what they were before the illumination. If these two ends are short circuited by a connecting a wire through a load, electrons flow from n- type to p-type semiconductor, giving us electrical energy. In Figure 23.5, the mechanism of electron/hole transfer across the interface of p- and n-type semiconductors is shown.

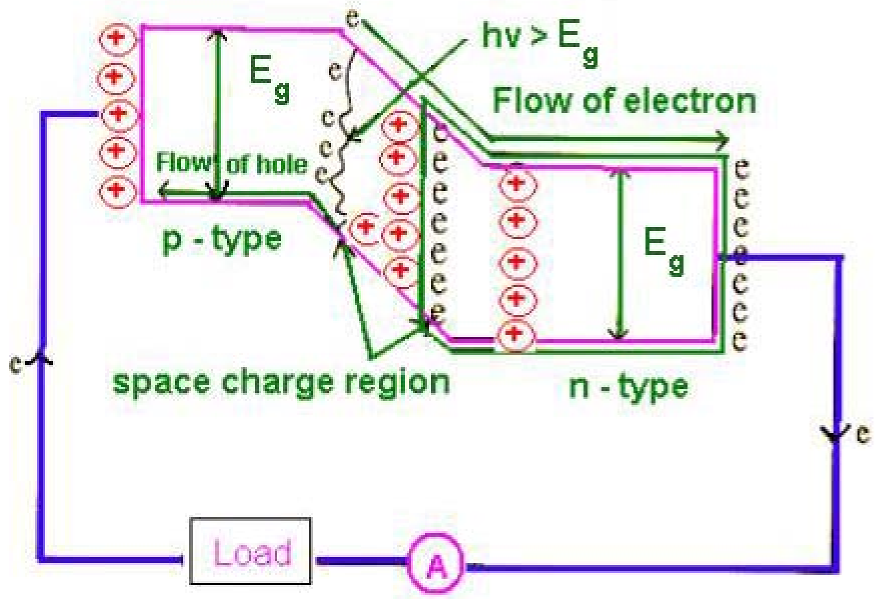

Figure 23.5 A schematic diagram of energy levels and electron/hole transfer across the p:n junction and creation of excess charges at the two ends of the n and p-type semiconductors. The flow of current through the load and the junction is also shown.

Table 23.1 some characteristics of silicon solar cells.

Parameters	**Values**
PV module efficiency (%)	15
Module cost (Rs / peak watt)	80
Plant life time	30 years
Energy cost (Rs/ kWh)	6
Photocurrent at peak power for a 12cm ^{2} cell	0.33 A
Photovoltage	0.44 V

The PV cells are normally made of 12 cm^2 area and generally, polycrystalline solar cells are circular in dimension, though square types are also being made. From these individual solar cells, a power module is made to get the desired wattage. For example, to get a power of 7.7 kW, the total number of solar cells will be 53000, of which 250 would be connected in series and 212 in parallel. Such a combination of solar cells is called a PV module. The module as explained above would need a total area 1028 ft ^{2} of which solar cells would occupy an area of 685 ft^2

(The circular solar cells will need more space than its own area i.e., 685 ft^2 to accommodate 53000 solar cells in a rectangular shape). In Figure 23.6, schematic arrangement of silicon solar module with load is shown to give an idea about the entire system of power utilization by solar energy.

The efficiency of a solar cell is calculated by measuring the total power generated by the solar cell divided by total power of light falling on the solar cells. For these calculations, normally solar intensity at noon is taken as a standard value, which is known as the peak power measured in the units of watt and is normally taken as 100 milliwatt /cm^2.

23.7 Problems

1) What are the distinguishing features between primary cells secondary cells, fuel cells and solar cells?

2) The lead acid battery (a secondary cell) can be recharged and reused for a few years after which it can not be recharged and reused. Can you think of reason why it can not be used any further ?

3) Propane (C_3H_8) can be used in a fuel cell and the combustion products are CO_2 and H_2O. Write a balanced chemical reaction for the combustion process. The standard free energy of combustion is -2108 kJ/mol of C_3H_8. Since five oxygen molecules (oxidation state zero) are reduced to the oxidation state of -2 , 20 electrons are involved in the process ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) What is the emf of the fuel cell ?

4) The standard free energies of combustion of CH_4 and CH_3OH are - 818 and -706.9 kJ/mol respectively. Calculate the emfs of these cells. The standard molar enthalpies for the combustion reactions are -890.4 and - 7640 kJ / mol. Defining the relative efficiencies of electrical vs thermal processes as

$E = \Delta G^o{}_m / \Delta H^o{}_m$. Calculate the values of E for CH_4 and CH_3OH

5) For a few common semiconductors, find out the excitation energy required to excite the electrons / holes so that they can conduct electricity.

6) Contrast the natural photosynthetic process with that of the processes occurring in a fuel cell and a solar cell.

Recap

In this Lecture you have learnt the following

SUMMARY

Primary cells, secondary cells and fuel cells are the major sources of electrical energy. In the case of secondary cells, the cell reaction producing electrical energy (discharge process) can be reversed by applying an external source of current (the charging process). In the case of primary cells, the discharge process is irreversible and cannot be reversed. In fuel cells, the chemical energy associated with the oxidation of fuels (reducing agents) is directly converted into electrical energy more efficiently than in other conventional processes. In photovoltaic solar cells, the light energy from sun is converted to electrical energy. Efforts to build rechargeable and reusable cells, environmentally friendly cells and pollution free batteries will always continue.

Very soon , cars running on fuel cells and solar cells on a large scale will become a reality.