C H A P T E R 9

Learning Objectives

ELECTRO-CHEMICAL POWER SOURCES

➤ Electrochemical cells convert chemical energy into electrical energy

9.1. Faraday's Laws of Electrolysis

From his experiments, Faraday deduced two fundamental laws which govern the phenomenon of electrolysis. These are :

(i)   First Law. The mass of ions liberated at an electrode is directly proportional to the quantity of electricity *i.e.* charge which passes through the electrolyte.

(ii) Second Law. The masses of ions of different substances liberated by the same quantity of electricity are proportional to their chemical equivalent weights.

Explanation of the First Law

Michael Faraday

If m = mass of the ions liberated, Q = quantity of electricity = $I \times t$ where I is the current and t is the time, then according to the first law $m \propto Q$ or $m = Z Q$ or $m = Z It$

where Z is a constant and is known as the electrochemical equivalent (*E.C.E.*) of the substance.

If $Q = 1$ coulomb *i.e.* $I = 1$ ampere and $t = 1$ second, then $m = Z$.

Hence, *E.C.E.* of a substance is *equal to the mass of its ions liberated by the passage of one ampere current for one second through its electrolytic solution or by the passage of a charge of one coulomb.*

In fact, the constant Z is composite and it depends on the valency and atomic weight of the substance concerned. Its value is given by $Z = \left(\dfrac{1}{F} \cdot \dfrac{a}{v} \right)$ where a is the atomic weight, v the valency

and F is Faraday's constant. It is so because m is proportional to atomic weight, since each ion carries a definite charge. Obviously, the charge carried by an ion is proportional to its valency. Now, consider the molecules of sulphuric acid and copper sulphate. The sulphion SO_4^- in the acid molecule is combined with two positive hydrogen ions, whereas in $CuSO_4$ molecule, it is combined only with one positive (bivalent) Cu^{++} ion. It is seen that a copper ion being bivalent carries twice the charge of a hydrogen ion which is univalent (monovalent). It means that in order to transfer a given quantity of electricity, only one-half as many bivalent copper ions as univalent hydrogen ions will be required. In other words, greater is the valency of an ion, smaller is the number of ions needed to carry a given quantity of electricity or charge which means that the mass of an ion liberated is inversely proportional to its valency.

$$\therefore \qquad\qquad m \;=\; \left(\frac{1}{F} \cdot \frac{a}{v} \right) It = \left(\frac{1}{F} \cdot \frac{a}{v} \right) Q = \frac{E}{F} \cdot Q$$

where E is the chemical equivalent weight ($= a/v$).

The constant F is known as Faraday's constant. The value of Faraday's constant can be found thus. It is found that one coulomb liberates 0.001118 gram of silver. Moreover, silver is univalent and its atomic weight is 107.88. Hence, substituting these values above, we find that

$$0.001118 \;=\; \frac{1}{F} \cdot 107.88 \times 1$$

$\therefore \quad F = 107.88 / 0.001118 = 96{,}500$ coulomb, which corresponds to $96{,}500/3600 = 26.8$ Ah

Faraday's constant is defined as *the charge required to liberate one gram-equivalent of any substance*.

For all substances, $\dfrac{\text{chemical equivalent } (E)}{\text{electrochemical equivalent } (Z)} =$ Faraday's constant $(F) = 96{,}500$ coulomb

or $F = E/Z$

Explanation of the Second Law

Suppose an electric current is passed for the same time through acidulated water, solution of $CuSO_4$ and $AgNO_3$, then for every 1.0078 (or 1.008) gram of hydrogen evolved, 107.88 gram of silver and 31.54 gram of Cu are liberated. The values 107.88 and 31.54 represent the equivalent weights* of silver and copper respectively *i.e.* their atomic weights (as referred to hydrogen) divided by their respective valencies.

Example 9.1. *Calculate the time taken to deposit a coating of nickel 0.05 cm thick on a metal surface by means of a current of 8 A per cm^2 of surface. Nickel is a divalent metal of atomic weight 59 and of density 9 gram/cm^3. Silver has an atomic weight of 108 and an E.C.E. of 1.118 mg/C.*

Solution. Wt. of nickel to be deposited per cm^2 of surface $= 1 \times 0.05 \times 9 = 0.45$ g

Now $\quad\quad\quad \dfrac{E.C.E. \text{ of } Ni}{E.C.E. \text{ of } Ag} = \dfrac{\text{chemical equivalent of } Ni}{\text{chemical equivalent of } Ag}$

$\therefore \quad\quad\quad E.C.E. \text{ of } Ni = 1.118 \times 10^{-3} \times \dfrac{(59/2)}{108} = 0.0003053$ g/C

(chemical equivalent $=$ atomic wt./valency)

Now $m = ZIt$ $\therefore$ $0.45 = 0.0003053 \times 8 \times t$; $t = 184$ second $=$ **3 min. 4 second**

Exmaple 9.2. *If 18.258 gm of nickel are deposited by 100 amp flowing for 10 minutes, how much copper would be deposited by 50 amp for 6 minutes : Atomic weight of nickel = 58.6 and that of copper 63.18. Valency of both is 2.* **(Electric Power AMIE Summer 1991)**

Solution. From Faraday's first law, we get $m = ZIt = m\left(\dfrac{1}{F} \cdot \dfrac{a}{v}\right)It.$

If m_1 is the mass of nickel deposited and m_2 that of copper, then

$$m_1 = 18.258 = \left(\dfrac{1}{F} \cdot \dfrac{58.6}{2}\right) \times 100 \ (10 \times 60), \left(\dfrac{1}{F} \cdot \dfrac{63.18}{2}\right) \times 50 \times (6 \times 60)$$

$\therefore \quad\quad\quad \dfrac{m_2}{18.258} = \dfrac{31.59}{29.3} \times \dfrac{18,000}{60,000} \quad\quad \therefore \ m_2 = $ **5.905 gm**

Example 9.3. *The cylindrical surface of a shaft of diameter 12 cm and length 24 cm is to be repaired by electrodeposition of 0.1 cm thick nickel on it. Calculate the time taken if the current used is 100 A. The following data may be used :*

Specific gravity of nickel = 8.9 ; Atomic weight of nickel = 58.7 (divalent) ; E.C.E. of silver = 1.2 mg/C; Atomic weight of silver = 107.9. **(Elect. Engg. A.M.Ae. S.I. June, 1991)**

Solution. Curved surface of the salt $= \pi D \times l = \pi \times 12 \times 24$ cm^2

Thickness of nickel layer $= 0.1$ cm

Volume of nickel to be deposited $= 12\pi \times 24 \times 0.1 = 90.5$ cm^3

Mass of nickel deposited $= 90.5 \times 8.9 = 805.4$ g

Chemical equivalent of $Ni = \dfrac{\text{atomic weight}}{\text{valency}} = \dfrac{58.7}{2} = 29.35$

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* The electro-chemical equivalents and chemical equivalents of different substance are inter-related thus :

$$\dfrac{E.C.E. \text{ of } A}{E.C.E. \text{ of } B} = \dfrac{\text{chemical equivalent of } A}{\text{chemical equivalent of } B}$$

Further, if m_1 and m_2 are masses of ions deposited at or liberated from an electrode, E_1 and E_2 their chemical equivalents and Z_1 and Z_2 their electrochemical equivalent weights, then

$$m_1/m_2 = E_1/E_2 = Z_1/Z_2$$

Now $\dfrac{E.C.E.\text{ of } Ni}{E.C.E.\text{ of } Ag} = \dfrac{\text{chemical equivalent of } Ni}{\text{chemical equivalent of } Ag}$

∴ $\dfrac{E.C.E.\text{ of } Ni}{1.12} = \dfrac{29.35}{107.9}$

∴ $E.C.E.\text{ of } Ni = 1.12 \times 29.35/107.9 = 0.305$ mg/C

Now $m = ZIt$

∴ $805.4 = 0.305 \times 10^{-3} \times 100 \times t$ ∴ $t = 26{,}406$ second or **7 hr, 20 min 7 s**

Example 9.4. *The worn-out part of a circular shaft 15 cm in diameter and 30 cm long is to be repaired by depositing on it 0.15 cm of Nickel by an electro-depositing process. Estimate the qunatity of electricity required and the time if the current density is to be 25 mA/cm². The current efficiency of the process may be taken as 95 per cent. Take E.C.E. for nickel as 0.3043 mg/coulomb and the density of nickel as 8.9 g/cm³.* **(Elect. Power-I, Bangalore Univ.)**

Solution. Curved surface area of shaft $= \pi D \times l = \pi \times 15 \times 30 = 1414$ cm².

Thickness of nickel layer $= 0.15$ cm

Volume of nickel to be deposited $= 1414 \times 0.15 = 212$ cm³

Mass of nickel to be deposited $= 212 \times 8.9 = 1887$ gram

Now, $m = ZQ; Q = m/Z = 1887/0.343 \times 10^{-3} = \mathbf{62 \times 10^5}$ **C**

Now, current density $= 15 \times 10^{-3}$ A/cm²; $A = 1414$ cm²

$I = 25 \times 10^{-3} \times 1414 = 35.35$ A

Since $Q = It$ ∴ $t = 62 \times 10^5/35.35 = 1.7 \times 10^5$ s = **47.2 hr.**

Example 9.5. *A refining plant employs 1000 cells for copper refining. A current of 5000 A is used and the voltage per cell is 0.25 volt. If the plant works for 100 hours/week, determine the annual output of refined copper and the energy consumption in kWh per tonne. The electrochemical equivalent of copper is 1.1844 kg/1000 Ah.*

(Electric Drives and Utilization, Punjab Univ. Jan. 1991)

Solution. Total cell voltage $= 0.25 \times 1000 = 250$ V; $I = 5000$ A; plant working time = 100 hour/week $= 100 \times 52 = 5200$ hour/year; $Z = 1.1844$ kg/1000 Ah; 1 Ah $= 1 \times 60 \times 60 = 3600$ C;

∴ $Z = 1.1844$ kg/1000 $\times 3600 = 0.329 \times 10^{-6}$ kg/C.

According to Faraday's law of Electrolysis, the amount of refined copper produced per year is

$m = Z I t = 0.329 \times 10^{-6} \times 5000 \times (5200 \times 3600) = 3079$ kg = **3.079 tonne.**

Hence, annual output of refined copper = 3.079 tonne

Energy consumed per year $= 250 \times 5000 \times 5200/1000 = 6500$ kWh

This is the energy consumed for refining 3.079 tonne of copper

∴ Energy consumed per tonne $= 6500/3.079 = $ **2110 kWh/tonne.**

Example 9.6. *A sheet of iron having a total surface area of 0.36 m² is to be electroplated with copper to a thickness of 0.0254 mm. What quantity of electricity will be required ? The iron will be made the cathode and immersed, together with an anode of pure copper, in a solution of copper sulphate.*

(Assume the mass density of copper $= 8.96 \times 10^3$ kg m⁻³; E.C.E. of copper —32.9 × 10⁻⁸ kg C¹ Current density = 300 Am⁻²) **(AMIE Sec. B Utilisation of Electric Power Summer 1992)**

Solution. Area over which copper is to be deposited = 0.36 m²

Thickness of the deposited copper $= 0.0254 \times 10^{-3}$ m

Volume of deposited copper $= 0.36 \times 0.0254 \times 10^{-3} = 9.144 \times 10^{-6}$ m³

Mass of copper deposited $= $ volume $\times$ density

$= 9.144 \times 10^{-6} \times 8.96 \times 10^3 = 0.0819$ kg

Now, $m = Z Q$ ∴ $Q = m/Z = 0.0819/32.9 \times 10^{-8} = $ **248936 C**

9.2. Polarisation of Back E.M.F.

Let us consider the case of two platinum electrodes dipped in dilute sulphuric acid solution. When a small potential difference is applied across the electrodes, no current is found to flow. When, however, the applied voltage is increased, a time comes when a temporary flow of current takes place. The H^+ ions move towards the cathodes and O⁻⁻ ions move towards the anode and are absorbed there. These absorbed ions have a tendency to go back into the electolytic solution, thereby leaving them as oppositely-charged electrodes. This tendency produces an e.m.f. that is in opposition to the applied voltage which is consequently reduced.

This opposing e.m.f. which is produced in an electrolyte due to the absorption of gaseous ions by the electrolyte from the two electrodes is known as the back e.m.f. of electolysis or polarisation.

The value of this back e.m.f. is different from different electrolytes. The minimum voltage required to decompose an electrolyte is called the *decomposition* voltage for that electrolyte.

9.3. Value of Back E.M.F.

For producing electrolysis, it is necessary that the applied voltage must be greater than the back e.m.f. of electrolysis for that electrolyte. The value of this back e.m.f. of electrolysis can be found thus :

Let us, for example, find the decomposition voltage of water. We will assume that the energy required to separate water into its constituents (*i.e.* oxygen and hydrogen) is equal to the energy liberated when hydrogen and oxygen combine to form water. Let H kcal be the amount of heat energy absorbed when 9 kg of water are decomposed into 1 kg of hydrogen and 8 kg of oxygen. If the electrochemical equivalent of hydrogen is Z kg/coulomb, then the passage of q coulomb liberates Zq kg of hydrogen. Now, H is the heat energy required to release 1 kg of hydrogen, hence for releasing Zq kg of hydrogen, heat energy required is HZq kcal to $JHZq$ joules. If E is the decomposition voltage, then energy spent in circulating q coulomb of charge is Eq joule. Equating the two amounts of energies, we have

$$Eq \ = \ JHZq \text{ or } E = JHZ$$

where J is 4200 joule/kcal.

The e.m.f. of a cell can be calculated by determining the two electrode potentials. The electrode potential is calculated on the assumption that the electrical energy comes entirely from the heat of the reactions of the constituents. Let us take a zinc electrode. Suppose it is given that 1 kg of zinc when dissolved liberates 540 kcal of heat and that the electrochemical equivalent of zinc is 0.338×10^{-6} kg/coulomb. As calculated above,

$$E \ = \ JHZ = 4200 \times 540 \times 0.338 \times 10^{-6} = 0.76 \text{ volt}$$

The electrode potentials are usually referred to in terms of the potential of a standard hydrogen electrode *i.e.* an electrode of hydrogen gas at normal atmospheric pressure and in contact with a normal acid solution. In table No. 9.1 are given the elctrode potentials of various elements as referred to the standard hydrogen electrode. The elements are assumed to be in normal solution and at atmospheric pressure.

In the case of Daniel cell having copper and zinc electrodes, the copper electrode potential with respect to hydrogen ion is $+ 0.345$ V and that of the zinc electrode is -0.758 V. Hence, the cell e.m.f. is $0.345 - (-0.758) = 1.103$ volt. The e.m.f. of other primary cells can be found in a similar way.

<div align="center">

Table No. 9.1

</div>

| *Electrode*	*Potential (volt)*	*Electrode*	*Potential (volt)*
Cadmium	-0.398	Mercury	$+0.799$
Copper	$+0.345$	Nickel	-0.231
Hydrogen	0	Potassium	-2.922
Iron	-0.441	Silver	$+0.80$
Lead	-0.122	Zinc	-0.758

Example 9.7. *Calculate the weight of zinc and MnO$_2$ required to produce I ampere-hour in a leclanche cell.*

Atomic weights : Mn, 55 ; O, 16 ; Zn, 65. E.C.E. of hydrogen = 1.04×10^{-8} kg/C.

Solution. 1 ampere-hour = 3600 A-s = 3600 C

Wt. of hydrogen liberated = $Zq = 1.04 \times 10^{-8} \times 3600 = 37.44 \times 10^{-6}$ kg

Now, the chemical reactions in the cell are
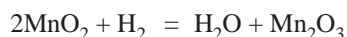
$$Zn + 2NH_4Cl = ZnCl_2 + 2NH_3 + H_2$$
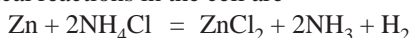
It is seen that 1 *atom* of zinc is used up in liberating *two atoms* of hydrogen. In other words, to produce 2 kg of hydrogen, 65 kg of zinc will have to go into chemical combination.

∴   Zinc required to produce 37.44×10^{-6} kg of hydrogen = $37.44 \times 10^{-6} \times 65/2$

$$= 1.217 \times 10^{-3} \text{ kg}$$

The hydrogen liberated combines with manganese dioxide as under :

$$2MnO_2 + H_2 = H_2O + Mn_2O_3$$

Atomic weight of   2 MnO$_2$ = $2(55 + 16 \times 2) = 174$

It is seen that 174 kg of MnO$_2$ combine with 2 kg of hydrogen, hence Wt. of MnO$_2$ needed to combine with 37.44×10^{-6} kg of hydrogen = $37.44 \times 10^{-6} \times 174/2 = 3.258 \times 10^{-3}$ kg.

Hence, for 1 ampere-hour, **1.217×10^{-3} kg** of zinc and **3.258×10^{-3} kg** of MnO$_2$ are needed.

Primary battery

9.4. Primary and Secondary Batteries

An electric battery consists of a number of electrochemical cells, connected either in series or parallel. A cell, which is the basic unit of a battery, may be defined as a power generating device, which is capable of converting stored chemical energy into electrical energy. If the stored energy is inherently present in the chemical substances, it is called a primary cell or a non-rechargeable cell. Accordingly, the battery made of these cells is called primary battery. The examples of primary cells are Leclanche cell, zinc-chlorine cell, alkaline-manganese cell and metal air cells etc.

Secondary battery

If, on the other hand, energy is induced in the chemical substances by applying an external source, it is called a secondary cell or rechargeable cell. A battery made out of these cells is called a secondary battery or storage battery or rechargeable battery. Examples of secondary cells are lead-acid cell, nickel-cadmium cell, nickel-iron cell, nickel-zinc cell, nickel-hydrogen cell, silver-zinc cell and high temperature cells like lithium-chlorine cell, lithium-sulphur cell, sodium-sulphur cell etc.

9.5. Classification of Secondary Batteries Based on Their Use

Various types of secondary batteries can be grouped in to the following categories as per their use :

1. *Automotive Batteries or SLI Batteries or Portable Batteries*

These are used for starting, lighting and ignition (*SLI*) in internal-combustion-engined vehicles. Examples are; lead-acid batteries, nickel-cadmium batteries etc.

2. *Vehicle Traction Batteries* or *Motive Power Batteries* or *Industrial Batteries*

These are used as a motive power source for a wide variety of vehicles. Lead-acid batteries, nickel-iron batteries, silver-zinc batteries have been used for this purpose. A number of advance batteries including high-temperature batteries are under development for electric vehicle (*EV*) use. These high-temperature batteries like sodium-sulphur and lithium-iron sulphide have energy densities in the range of 100-120 Wh/kg.

3. *Stationary Batteries.*

These fall into two groups (*a*) standby power system which is used intermittently and (*b*) load-levelling system which stores energy when demand is low and, later on, uses it to meet peak demand.

9.6. Classification of Lead Storage Batteries

Lead storage batteries may be classified according to the service which they provide.

1. *SLI Batteries*

The primary purpose of these batteries is to supply power for engine starting, lighting and ignition (*SLI*) of vehicles propelled by IC engines such as automobiles, buses, lorries and other heavy road vehicles and motor cycles etc. Usually, these batteries provide 12 V and consist of six series-connected lead-acid cells with capacity of the other of 100 Ah. Their present-day energy density is about 45 Wh/kg and 75 Wh/dm^3.

These days 'maintenance-free' (*MF*) *SLI* batteries have been designed, which do not require the addition of water

H_2SO_4 (electrolyte)

Lead grid packed with spongy lead (anode)

Lead grid packed with PbO_2(cathode)

Lead storage batteries

throughout their normal service life of 2-5 years. *MF* versions of the *SLI* batteries are constructed of such material that no gassing occurs during charging. In *MF* batteries, the electrolyte is either absorbed within the microporous separators and the plates or is immobilized with suitable gelling agents.

These days the *SLI* battereis are charged from an alternator (*AC* generator) and not from dynamo (*DC* generator). The alternating current produced by the alternator is converted into direct current by
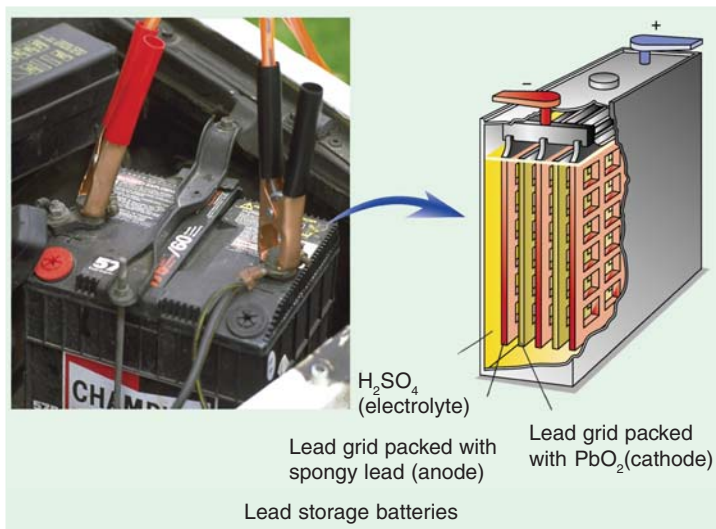
a full-wave bridge rectifier, which uses semi-conductor diodes. In this arrangement, no cutout is needed and the transistorised voltage controller regulates the alternator output to suit the electrical load and the state of charge of the battery. The battery is charged under constant-voltage conditions.

2.   *Vehicle Traction Batteries*

The recent universal concern over the levels of toxic gases (particularly in urban areas) emitted by the *IC* engines has revived interest in electric traction. There has been great development in the use of battery-powered vehicles, primarily industrial trucks and commercial road vehicles of various types like 'milk floats' (*i.e.* bottled-milk delivery trucks), fork lift trucks, mining, airport tractors, aircraft service vehicles, electric cars and, more recently, in robotics and guided vehicles.

Traction batteries are of higher quality than *SLI* batteries. They provide constant output voltage, high volumetric capacity, good resistance to vibration and a long service life. They can withstand prolonged and deep discharges followed by deep recharges usually on a daily basis. The voltage of traction batteries varies from 12 V to 240 V and they have a cycle life of 1000-1500 cycles.

A number of advanced batteries and under development for *EV* use (*i*) room temperature batteries like zinc-nickel oxide battery (75 Wh/kg) and zinc-chlorine hydrate battery (80 Wh/kg) and (*ii*) high-temperature batteries like sodium-sulphur battery (120 Wh/kg) and lithium-iron sulphide battery (100 Wh/kg).

3.   *Stationary Batteries*

Their use falls into two groups :

(*a*) as standby power system and (*b*) as load-levelling system.

In the standby applications, the battery is used to power essential equipment or to provide alarms or emergency lighting, in case of break-down in the main power supply. Standby applications have increased in recent years with increasing demand for uninterruptable power systems (*UPS*) and a tremendous growth in new telecommunication networks. The *UPS* provides 'clean' a.c supply free of sage or surges in the line voltage, frequency variations, spikes and transients to modern computer and electronic equipment. Banks of sealed lead-acid (*SLA*) standby batteries have been recently used in telecommunication systems and for *UPS* applications.

Recently, advanced lead-acid batteries have been used for load-levelling purpose in the electric generating plants. A 100 M Wh lead-acid battery load-levelling system could occupy a building two and a half storey high and an area of about 250,000 m^2.

9.7. Parts of a Lead-acid Battery

A battery consists of a number of cells and each cell of the battery-consists of (*a*) positive and negative plants (*b*) separators and (*c*) electrolyte, all contained in one of the many compartments of the battery container.* Different parts of a lead-acid battery are as under :

(*i*) *Plates.* A plate consists of a lattice type of grid of cast antimonial lead alloy which is covered with *active* material (Art. 9.8). The grid not only serves as a support for the fragile active material but also conducts electric current. Grid for the positive and negative plates are often of the same design although negative plate grids are made somewhat lighter. As discussed in Art. 9.10, positive plates are usually Plante plates whereas negative plates are generally of Faure or pasted type.

(*ii*) *Separators.* These are thin sheets of a porous material placed between the positive and negative plates for preventing contact between them and thus avoiding internal short-circuiting of the battery. A separator must, however, be sufficiently porous to allow diffusion or circulation of electrolyte between the plates. These are made of especially-treated cedar wood, glass wool mat, microporous rubber (mipor), microporous plastics (plastipore, miplast) and perforated p.v.c. as shown in Fig. 9.1. In addition to good porosity, a separator must possess high electrical resistance and mechanical strength.

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*   The most common form of lead-acid cell used for marine applications is the tubular cell which consists of 'armoured' tubular positive plate of standard flat negative plate.

(*iii*) *Electrolyte.* It is dilute sulphuric acid which fills the cell compartment to immerse the plates completely.
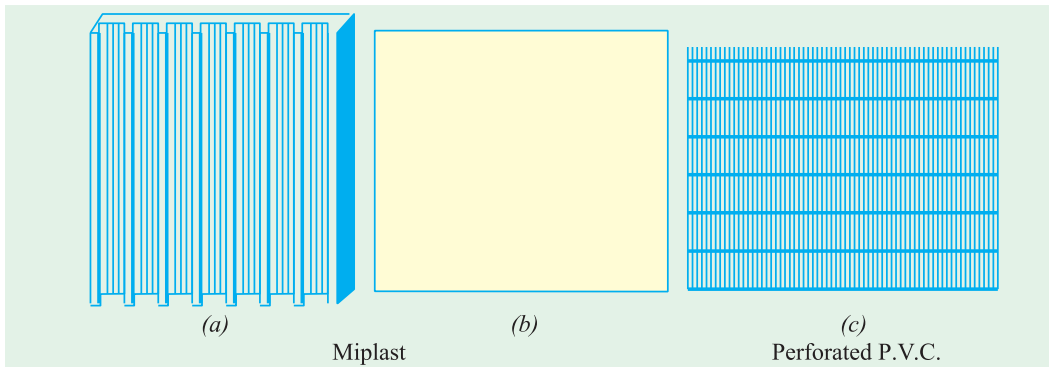

(a)	*(b)*	*(c)*
Miplast		Perforated P.V.C.

Fig. 9.1

(*iv*) *Container.* It may be made of vulcanised rubber or moulded hard rubber (ebonite), moulded plastic, ceramics, glass or celluloid. The vulcanised rubber containers are used for car service, while glass containers are superior for lighting plants and wireless sets. Celluloid containers are mostly used for portbable wireless set batteries. A single monoblock type container with 6 compartments generally used for starting batteries is shown in Fig. 9.2. Full details of a Russian 12-CAM-28 lead-acid battery parts are shown in Fig. 9.3. Details of some of these parts are as follows:
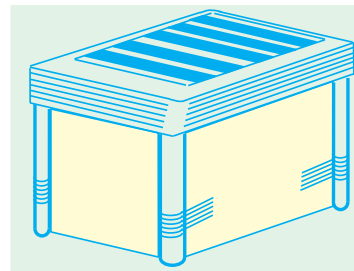

Fig. 9.2

(*a*) *Bottom Grooved Support Blocks.* These are raised ribs, either fitted in the bottom of the container or made with the container itself. Their function is to

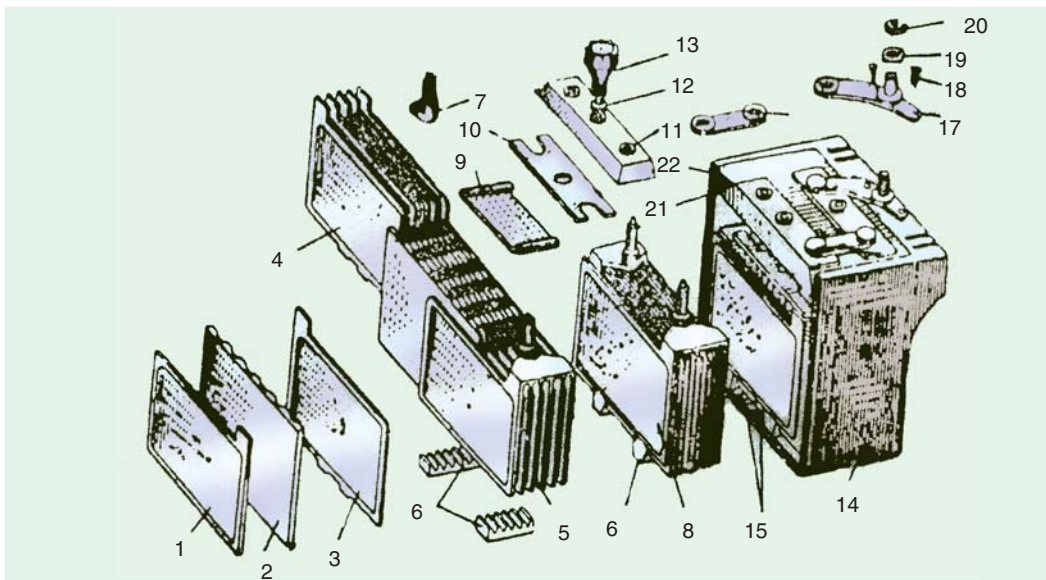**Fig. 9.3.** (Courtesy MIR Publishers. Moscow)

1. −ve plate 2. separator 3. + ve plate. 4. + ve group 5. −ve group 6. −ve group grooved support block 7. lug 8. plate group 9. guard screen 10. guard plate 11. cell cover 12. plug washer 13. vent plug 14. monoblock jar 15. supporting prisms of + ve group 16. inter-cell connector 17. terminal lug 18. screw 19. washer 20. nut 21. rubber packing 22. sealing compound.

support the plates and hold them in position and at the same time protect them from short-circuits that would otherwise occur as a result of fall of the active material from the plates onto the bottom of the container.

(*b*) *Connecting Bar.* It is the lead alloy link which joins the cells together in series connecting the positive pillar of one cell to the negative pillar of the next one.

(*c*) *Terminal Post* or *Pillar*. It is the upward extension from each connecting bar which passes through the cell cover for cable connections to the outside circuits. For easy indentification, the negative terminal post is smaller in diameter than the positive terminal post.

(*d*) *Vent Plugs* or *Filler Caps.* These are made of polystyrene or rubber and are usually screwed in the cover. Their function is to prevent escape of electrolyte but allow the free exit of the gas. These can be easily removed for topping up or taking hydrometer readings.

(*e*) *External Connecting Straps.* These are the antimonial lead alloy flat bars which connect the positive terminal post of one cell to the negative of the next across the top of the cover. These are of very solid construction especially in starting batteries because they have to carry very heavy currents.

9.8. Active materials of a Lead-acid Cell

Those substances of the cell which take active part in chemical combination and hence absorb or porduce electricity during charging or discharging, are known as *active materials* of the cell.

The active materials of a lead-acid cell are :

1. *Lead peroxide* (PbO_2) for + ve plate **2.** *Sponge Lead* (Pb) for −ve plate **3.** *Dilute Sulphuric Acid* (H_2SO_4) as electrolyte.

1. Lead Peroxide

It is a combination of lead and oxygen, is dark chocolate brown in colour and is quite hard but brittle substance. It is made up of one atom of lead (Pb) and two atoms of oxygen (O_2) and its chemical formula is PbO_2. As said earlier, it forms the positive active material.

2. Sponge Lead

It is pure lead in soft sponge or porous condition. Its chemical formula is Pb and forms the negative active material.

3. Dilute Sulphuric Acid

It is approximately 3 parts water and one part sulphuric acid. The chemical formula of the acid is H_2SO_4. The positive and negative plates are immersed in this solution which is known as electrolyte. It is this medium through which the current produces chemical changes.

Hence, the lead-acid cell depends for its action on the presence of two plates covered with PbO_2 and Pb in a solution of dilute H_2SO_4 of specific gravity 1.21 or nearabout.

Lead in the form of PbO_2 or sponge Pb has very little mechanical strength, hence it is supported by plates of pure lead. Those plates covered with or otherwise supporting PbO_2 are known as + ve plates and those supporting sponge lead are called −ve plates. The + ve and −ve plates are arranged alternately and are connected to two common +ve and −ve terminals. These plates are assembled in a suitable jar or container to make a complete cell as discussed in Art. 9.4 above.

9.9. Chemical changes

(*i*) DISCHARGING (Fig. 9.4)

When the cell is fully charge, its positive plate or anode is PbO_2 (dark chocolate brown) and the negative plate or cathode is Pb (slate grey). When the cell discharges *i.e.* it sends current through the external load, then H_2SO_4 is dissociated into positive H_2 and negative SO_4 ions. As the current within the cell is flowing from cathode to anode, H_2 ions move to anode and SO_4 ions move to the cathode.

At anode (PbO_2), H_2 combines with the oxygen of PbO_2 and H_2SO_4 attacks lead to form $PbSO_4$.

$$PbO_2 + H_2 + H_2SO_4 \longrightarrow PbSO_4 + 2H_2O$$
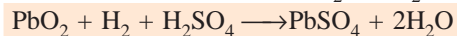
At the cathode (Pb), SO_4 combines with it to form $PbSO_4$
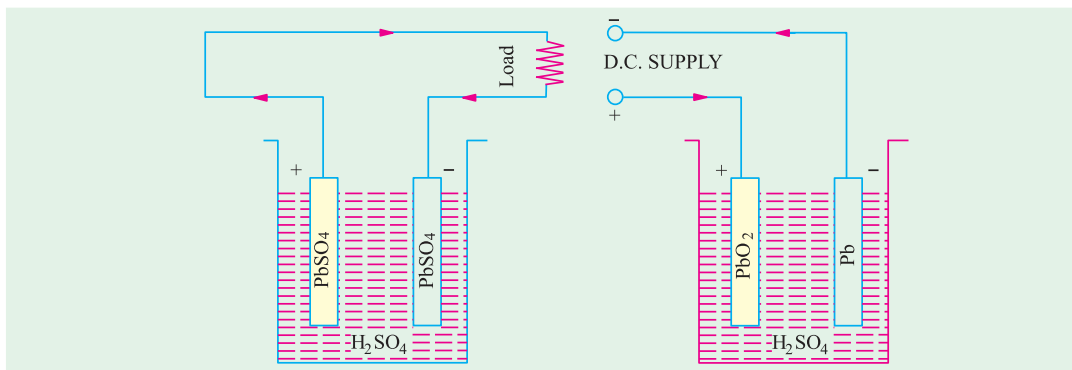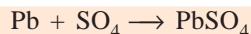
$$Pb + SO_4 \longrightarrow PbSO_4$$


Fig. 9.4   **Fig. 9.5**

It will be noted that during discharging :

  (*i*) *Both anode and cathode become $PbSO_4$ which is somewhat whitish in colour.*

 (*ii*) *Due to formation of water, specific gravity of the acid decreases.*

(*iii*) *Voltage of the cell decreases.* (*iv*) *The cell gives out energy.*

(*ii*) **CHARGING (Fig. 9.5)**

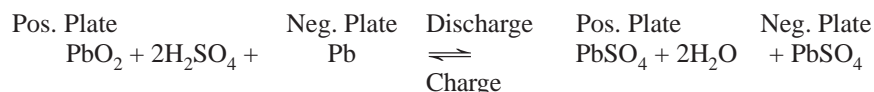   When the cell is recharged, the H_2 ions move to cathode and SO_4 ions go to anode and the following changes take place :

    At Cathode $PbSO_4 + H_2 \longrightarrow Pb + H_2SO_4$

    At Anode $PbSO_4 + 2H_2O \longrightarrow PbO_2 + 2H_2SO_4$
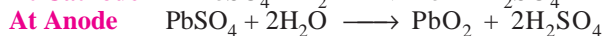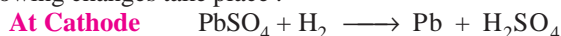
    Hence, the anode and cathode again become PbO_2 and Pb respectively.

  (*i*) *The anode becomes dark chocolate brown in colour (PbO_2) and cathode becomes grey metallic lead (Pb).*

 (*ii*) *Due to consumption of water, specific gravity of H_2SO_4 is increased.*

(*iii*) *There is arise in voltage.* (*iv*) *Energy is absorbed by the cell.*

    The charging and discharging of the cell can be represented by a single reversible equation given below :

       Pos. Plate   Neg. Plate   Discharge   Pos. Plate   Neg. Plate

          $PbO_2 + 2H_2SO_4 +$ Pb $\rightleftharpoons$ $PbSO_4 + 2H_2O$ $+ PbSO_4$

                                           Charge

    For discharge, the equation should be read from left to right and for charge from right to left.

    Example 9.8. *Estimate the necessary weight of active material in the positive and negative plates of a lead-acid secondary cell per ampere-hour output* (*atomic weight of lead 207, valency 2, E.C.E. of hydrogen 0.0104 × 10⁻⁶ kg/C*).

    Solution. Wt. of hydrogen evolved per ampere-hour $= 0.0104 \times 10^{-6} \times 3{,}600$

                                      $= 37.44 \times 10^{-6}$ kg

During discharge, reaction at cathode is $Pb + H_2SO_4 = PbSO_4 + H_2$

As seen, 207 kg of lead react chemically to liberate 2 kg of hydrogen.

Hence, weight of Pb needed per ampere-hour $= 37.44 \times 10^{-6} \times 207/2 = 3.876 \times 10^{-3}$ kg

At anode the reaction is : $PbO_2 + H_2 \longrightarrow PbO + H_2O$

Atomic weight of $PbO_2 = 207 + 32 = 239$

∴Wt. of PbO_2 going into combination per ampere-hour $= 37.44 \times 10^{-6} \times 239/2 = $ **4.474×10^{-3} kg**

Therefore, quantity of active material required per ampere-hour is : lead **3.876×10^{-3} kg** and lead peroxide **4.474×10^{-3} kg.**

9.10. Formation of Plates of Lead-acid Cells

There are, in general, two methods of producing the active materials of the cells and attaching them to lead plates. These are known after the names of their inventors. **(1) Plante** plates or formed plates **(2) Faure** plates or pasted plates.

9.11. Plante Process

In this process, two sheets of lead are taken and immersed in dilute H_2SO_4. When a current is passed into this lead-acid cell from a dynamo or some other external source of supply, then due to electrolysis, hydrogen and oxygen are evolved. At anode, oxygen attacks lead converting it into PbO_2 whereas cathode is unaffected because hydrogen can form on compound with Pb.

If the cell is now discharged (or current is reversed through it), the peroxide-coated plate becomes cathode, so hydrogen forms on it and combines with the oxygen of PbO_2 to form water thus :

$$PbO_2 + 2H_2 \longrightarrow Pb + 2H_2O$$
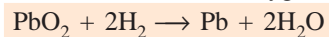
At the same time, oxygen goes to anode (the plate previously unattacked) which is lead and reacts to form PbO_2. Hence, the anode becomes covered with a thin film of PbO_2.

By continuous reversal of the current or by charging and discharging the above electrolytic cell, the thin film of PbO_2 will become thicker and thicker and the polarity of the cell will take increasingly longer time to reverse. Two lead plates after being subjected to hundreds of reversals will acquire a skin of PbO_2 thick enough to possess sufficiently high capacity. This process of making positive plates is known as *formation*. The negative plates are also made by the same process. They are turned from positive to negative plates by reversing the current through them until whole PbO_2 is converted into sponge lead. Although Plante positives are very commonly used for stationary work, Plante negatives have been completely replaced by the Faure or pasted type plates as discussed in Art. 9.13. However, owing to the length of time required and enormous expenditure of electrical energy, this process is commercially impracticable. The process of formation can be accelerated by forming agents such as acetic, nitric or hydrochloric acid or their salts but still this method is expensive and slow and plates are heavy.

9.12. Structure of Plante Plates

It is seen that since active material on a Plante plate consists of a thin layer of PbO_2 formed on and from the surface of the lead plate, it must be made of large superficial area in order to get an appreciable volume of it. An ordinary lead plate subjected to the forming process as discussed above will have very small capacity. Its superficial area and hence its capacity, can be increased by grooving or laminating. Fig. 9.6 shows a Plante positive plate which consists of a pure lead grid with finely laminated surfaces. The construction of these plates consists of a large number of thin vertical laminations which are strengthened at intervals by horizontal binding ribs. This results in an increase of the superifical area 10 to 12 times that possessed by a plain lead sheet of the same overall dimensions. The above design makes possible the expansion of the plate structure to accommodate the increase in mass and the value of the active material (PbO_2) which takes place when the cell goes through a series of chemical changes during each cycle of charge or discharge. The expansions of the plate structure takes place downwards where there is room left for such purpose. Usually, a Plante positive plate expands by about 10% or so of its length during the course of its useful life.

Another type of Plante positive plate is the 'rosette' plate which consists of a perforated cast grid or framework of lead alloy with 5 to 12 per cent of antimony holding rosettes or spirals of corrugated pure lead tape. The rosettes (Fig. 9.7) provide the active material of the positive plate and, during formation, they expand in the holes of the grid which are countersunk on both sides of the grid. The advantages of such plates are that the lead-antimony grid is itself unaffected by the chemical action and the complete plate is exceptionally strong.

Other things being equal, the life of a Plante plate is in direct proportion to the weight of lead metal in it, because as the original layer of PbO_2 slowly crumbles away during the routing charging

and discharging of the cell, fresh active material is formed out of the underlying lead metal. Hence, the capacity of such a plate lasts as long as the plate itself. In this respect, Plante plate is superior to the Faure or pasted plate.
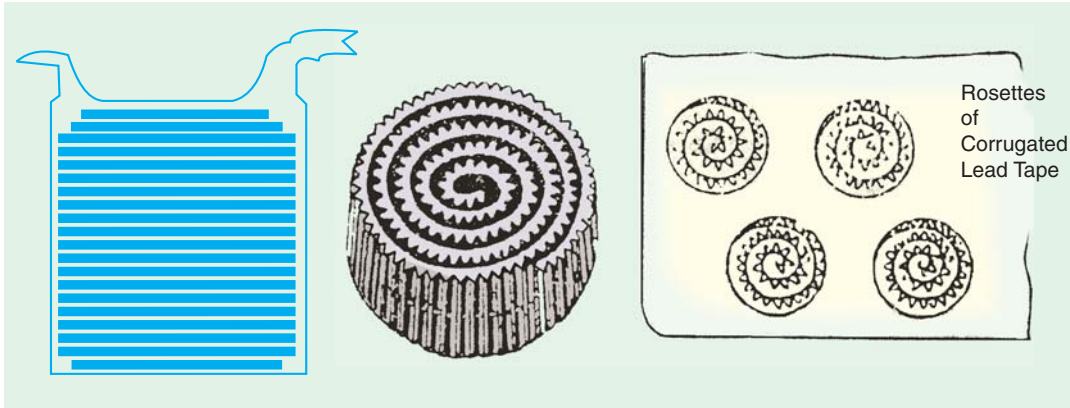

| **Fig. 9.6** | **Fig. 9.7** | **Fig 9.8** |

9.13. Faure Process

In the making of Faure plates, the active material is mechanically applied instead of being electrochemically produced out of lead plate itself as in Plante process. The active material which is in the form of red lead (Pb_3O_4) or litharge PbO or the mixture of the two in various proportions, is pressed into the interstices of a thin lead grid or lattice work of intersecting ribs which also serves as conductor of current. The plates after being thus pasted are allowed to dry and harden, are then assembled in weak solution of H_2SO_4 of specific gravity 1.1 to 1.2 and are formed by passing an electric current between them. If plates are meant to be positive, they are connected up as anodes, if negative, then as cathodes. The oxygen evolved at the anode converts the lead oxide (Pb_3O_4) into peroxide (PbO_2) and at cathode the hydrogen reduces PbO to sponge lead by abstracting the oxygen.

9.14. Positive Pasted Plates

Formation of positive plate involves converting lead oxide into PbO_2. A high lead oxide like Pb_3O_4 is used for economy both in current and time, although in practice, a mixture of Pb_3O_4 and PbO is taken-the latter being added to assist in the setting or cementation of the plate.

9.15. Negative Pasted Plates

Faure process is much better adopted for making a negative rather than a positive plate. The negative material *i.e.* sponge lead is quite tough instead of being hard and brittle like PbO_2 and, moreover, it undergoes a comparatively negligible change in volume during the charging and discharging of the cell. Hence, it has no tendency to disintegrate or shed out of the grid although it does tend to lose its porosity and become dense and so lose capacity. Hence, in the manufacture of the pasted negatives, a small percentage of certain substances like powdered pumic or graphite or magnesium sulphate or barium sulphate is added to increase the porosity of the material. If properly handled, a paste made with H_2SO_4, glycerine and PbO (or mixture of PbO and Pb_3O_4) results in a very good negative, because glycerine is carbonised during formation and so helps in keeping the paste porous.

Faure plates are in more general use because they are cheaper and have a high (capacity/weight) ratio than Plante plates. Because of the lightness and high capacity/weight ratio, such plates are used

practically for all kinds of portable service like electric vehicles, train lighting, car-lighting and strating etc. But their life is shorted as compared to Plante plates.

9.16. Structure of Faure Plates

Usually, the problem of Faure type grid is relatively simple as compared to the Plante type. In the case of Faure plates, the grid serves simply as a support for the active material and a conductor for the current and as a means for distributing the current evenly over the active material. Unlike Plante plates, it is not called upon to serve as a kind of reservoir from which fresh active material is continuosly being formed for replacing that which is lost in the wear and tear of service. Hence, this makes possible the use of an alloy of lead and antimony which, as pointed out earlier, resists the attack of acid and 'forming' effect of current more effectively than pure lead and is additionally much harder and stiffer.

Because of the hardening effect of antimony, it is possible to construct very thin light plates which possess sufficient rigidity to withstand the expensive action of the positive active material. Simplest type of grid consists of a meshwork of veritcal and horizontal ribs intersecting each other thereby forming a number of rectangular spaces in which the paste can be pressed and allowed to set. Such a thin grid has the disadvantage that there is not much to 'key' in the paste and due to a great shock or vibration the pellets are easily 'started' and so fall out.

A much better support to the active material can be given by the construction illustrated in Fig. 9.9 which is known as 'basket' type or screened grid. The paste instead of being is isolated pellets forms a continuous sheet contained and supported by the horizontal ribs of the gird. With this arrangement the material can be very effectively keyed in.

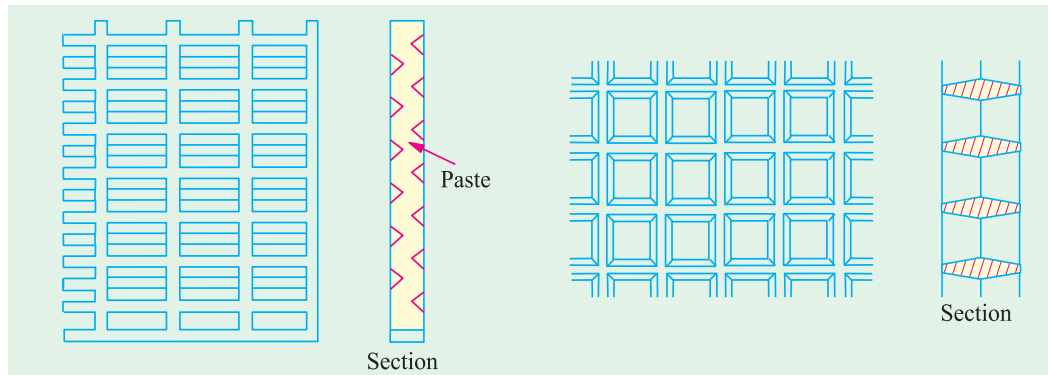Another type of grid structure used in pasted plates is shown in Fig. 9.10.

Fig. 9.9   **Fig. 9.10**

9.17. Comparison : Plante and Faure Plates

1. Plante plates have a longer life and can withstand rapid discharging (as in traction work) better than Faure's.
2. They are less liable to disintegration when in use then Faure's plates.
3. They are heavier and more expensive than Faure plates.
4. Plante plates have less capacity-to-weight ratio, values being 12 to 21 Ah per kg of plate, the corresponding values for Faure plate being 65 to 90 Ah/kg.

9.18. Internal Resistance and Capacity of a Cell

The secondary cell possesses internal resistance due to which some voltage is lost in the form of potential drop across it when current is flowing. Hence, the internal resistance of the cell has to be kept to the minimum.

One obvious way to lessen internal resistance is to increase the size of the plates. However, there

is a limit to this because the cell will become too big to handle. Hence, in practice, it is usual to multiply the number of plate inside the cell and to join all the negative plates together and all the positives ones together as shown in Fig. 9.11.

The effect is equivalent to joining many cells in parallel. At the same time, the length of the electrolyte between the electrodes is decreased with a consequent reduction in the internal resistance.

The 'capacity' of a cell is given by the product of current in amperes and the time in hours during which the cell can supply current until its e.m.f. falls to 1.8 volt. It is expressed in ampere-hour (Ah).

(a)   *(b)*

Fig. 9.11

The interlacing of plates not only decreases the internal resistance but additionally increases the capacity of the cell also. There is always one more negative plate than the positive paltes *i.e.* there is a negative plate at both ends. This gives not only more mechanical strength but also assures that both sides of a positive plate are used.

Since in this arrangement, the plates are quite close to each other, something must be done to make sure that a positive plate does not touch the negative plate otherwise an internal short-circuit will take place. The separation between the two plates is achieved by using separators which, in the case of small cells, are made of treated cedar wood, glass, wool mat, microporous rubber and mocroporous plastic and in the case of large stationary cells, they are in the form of glass rods.
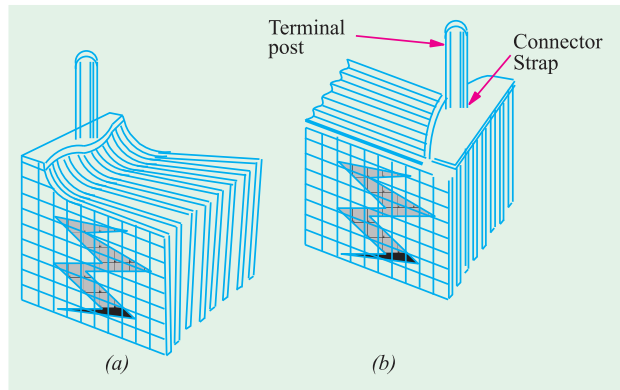
9.19. Two Efficiencies of the Cell

The efficiency of a cell can be considered in two ways :
   1. *The quantity or ampere-hour (Ah) efficiency*
   2. *The energy or watt-hour (Wh) efficiency*

The Ah efficiency does not take into account the varying voltages of charge and discharge. The Wh efficiency does so and is always less than Ah efficiency because average p.d. during discharging is less than that during charging. Usually, during discharge the e.m.f. falls from about 2.1 V to 1.8 V whereas during charge it rises from 1.8 volt to about 2.5 V.

$$\text{Ah efficiency} = \frac{\text{amp-hour discharge}}{\text{amp-hour charge}}$$

The Ah efficiency of a lead-acid cell is normally between 90 to 95%, meaning that about 100 Ah must be put back into the cell for every 90-95 Ah taken out of it. Because of gassing which takes place during the charge, the Ah available for delivery from the battery decreases. It also decreases (*i*) due to self-discharge of the plates caused due to local reactions and (*ii*) due to leakage of current because of faulty insulation between the cells of the battery.

The Wh efficiency varies between 72-80%.

If Ah efficiency is given, Wh efficiency can be found from the following relation :

$$\text{Wh efficiency} = \text{Ah efficiency} \times \frac{\text{average volts on discharge}}{\text{average volts on charge}}$$

From the above, it is clear that anything that increases the charge volts or reduces the discharge volts will decrease Wh efficiency. Because high charge and discharge rates will do this, hence it is advisable to avoid these.

9.20. Electrical Characteristics of the Lead-acid Cell

The three important features of an accumulator, of interests to an engineer, are (**1**) voltage (**2**) capacity and (**3**) efficiency.

1. Voltage

The open-circuit voltage of a fully-charged cell is approximately 2.2 volt. This value is not fixed but depends on (*a*) length of time since it was last charged (*b*) specific gravity-voltage increasing with increase in sp. gravity and *vice versa*. If sp. gravity comes near to density of water *i.e.* 1.00 then voltage of the cell will disappear altogether (*c*) temperature-voltage increases, though not much, with increase in temperature.

Fig. 9.12

The variations in the terminal p.d. of a cell on charge and discharge are shown in Fig. 9.12. The voltage-fall depends on the rate of discharge. Rates of discharge are generally specified by the number of hours during which the cell will sustain the rate in question before falling to 1.8 V. The voltage falls rapidly in the beginning (rate of fall depending on the rate of discharge), then vary slowly up to 1.85 and again suddenly to 1.8 V.

The voltage should not be allowed to fall to lower than 1.8 V, otherwise hard insoluble lead sulphate is formed on the plate which increases the internal resistance of the cell.

The general form of the voltage-time curves corresponding to 1-, 3- 50 and 10- hour rates of corresponding to the steady currents which would discharge the cell in the above mentioned times (in hour). It will be seen that both the terminal voltage and the rate at which the voltage and the rate at which the voltage falls, depend on the rate of discharge. The more rapid fall in voltage at higher rates of discharge is due to the rapid increase in the internal resistance of the cell.

During charging, the p.d. increases (Fig. 9.12). The curve is similar to the discharge curve reversed but is everywhere higher due to the increased density of H_2SO_4 in the pores of the positive plate.

Fig. 9.13

2. Capacity

It is measured in amp-hours (Ah). The capacity is always given at a specified rate of discharge (10-hour discharge in U.K., 8-hour discharge in U.S.A.). However, motor-cycle battery capacity is based on a 20-hour rate (at 30° C). The capacity depends upon the following :

(*a*) *Rate of discharge.* The capacity of a cell, as measured in Ah, depends on the discharge rate. It decreases with increased rate of discharge. Rapid rate of discharge means greater fall in p.d. of the cell due to internal resistance of the cell. Moreover, with rapid discharge the weakening of the acid in the pores of the plates is also greater. Hence, the chemical change produced at the plates by 1 ampere for 10 hours is not the same as produced by 2 A for 5 hours or 4 A for 2.5 hours. It is found that a cell having a 100 Ah capacity at 10 hour discharge rate, has its capacity reduced to 82.5 Ah at 5-hour rate and 50 Ah at 1-hour rate. The variation of capacity with discharge rate is shown in Fig. 9.14.
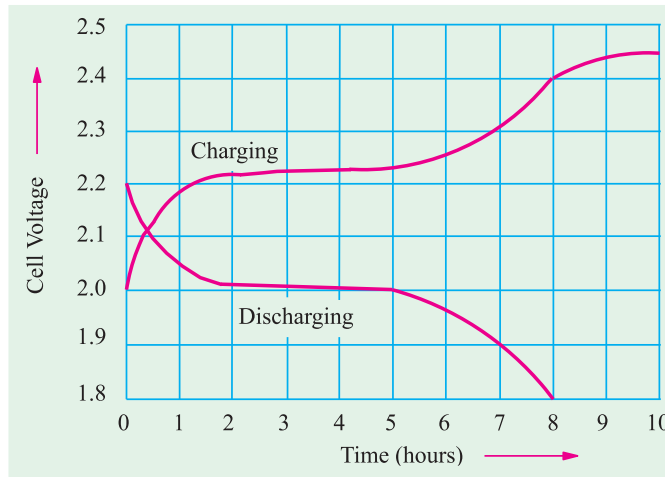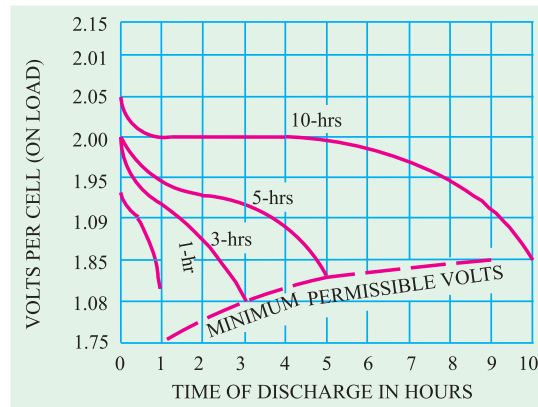
(*b*) *Temperature.* At high temperature,

(*i*) chemical reactions within the cell take place more vigorously.

(*ii*) the resistance of the acid is decreased and

(*iii*) there is a battery diffusion of the electrolyte.

Hence, high temperature increases the capacity of the lead-acid cell. Apparently, it is better to operate the battery at a high temperature. However, at high temperatures :

(*a*) the acid attacks the antimony-lead alloy grid, terminal posts and wooden separators.

Fig. 9.14

(*b*) the paste is rapidly changed into lead sulphate. Sulphation is always accompanied by expansion of paste particularly at the positive plates and results in buckling and cracking of the grid.

Hence, it is not advisable to work batteries above 40° C.

As temperature is lowered, the speed of chemical reactions is decreased. Moreover, cell resistance also increases. Consequently, the capacity of the cell decreases with decrease in temperature till at freezing point the capacity is reduced to zero even though the battery otherwise be fully charged.

(*c*) *Density of electrolyte.* As the density of electrolyte affects the internal resistance and the vigour of chemical reaction, it has an important effect on the capacity. Capacity increases with the density.

(*d*) *Quantity of active material.* Since production of electricity depends on chemical action taking place within the cells, it is obvious that the capacity of the battery must depend directly upon the kind and amount of the active material employed. Consider the following calculations:

The gram-equivalent of lead is 103.6 gram and Faraday's constant is 96,500 coulombs which is = 96,500/3600 = 26.8 Ah. Hence, during the delivery of one Ah by the cell, the quantity of lead expended to form lead sulphate at the negative plate is 103.6/26.8 = 3.86 gram.

Similarly, it can be calculated that, at the same time, 4.46 gram of PbO_2 would be converted into lead sulphate at the positive plate while 3.66 gram of acid would be expended to form 0.672 gram of water. It is obvious that for obtaining a cell of a greater capacity, it is necessary to provide the plates with larger amounts of active material.

3. Efficiency

It has already been discussed in Art. 9.19

9.21. Battery Ratings

Following standards have been adopted, both by industry and government organisations to get a fair picture of battery quantity :

1. Ampere-hour Capacity

It is a function of the total plate area *i.e.* size of the individual plate multiplied by the number of plates. For measuring this capacity, the battery is discharged continuously for 20 hours and its current output supplied to a standard load is measured. Suppose that a battery delivers 4A current for 20 hours. Hence, its rating is 80 Ah which is stamped on the battery case.

2. Reserve Capacity

It is one of the newly-developed rating standards and is more realistic because it provides a double-check on the Ah figures. The capacity is given by the number of minutes a battery will tolerate a 25 A drain without dropping below 10.5 V. Higher this rating, better the battery.
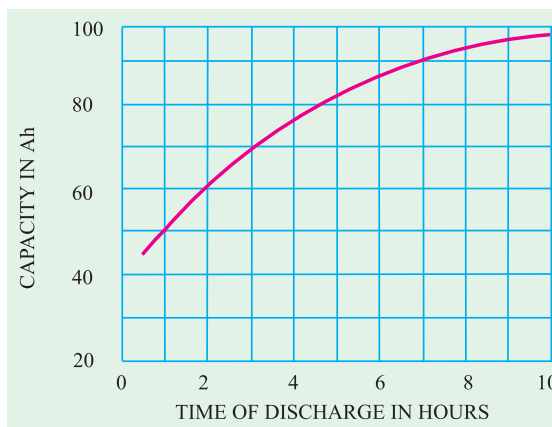
3.   Zero Cranking Power

It was the first cold weather rating and is applicable in relation to crafts which ply in freezing weather. This zero-degree performance test gives a valuable insight into battery quality. Large batteries are tested at a 300 A drain with battery chilled to –18°C (0°F) whereas smaller sizes are tested at half this value.

This test consists of two part (*a*) the battery is first chilled to –18°C (0°F) and the load applied for 5 second. Meanwhile, the voltage output is recorded. It is the first part of the zero-cranking-power rating. (*b*) The test is continued further till voltage drops to 5 V. The number of minutes it takes to reduce the voltage to 5 V forms the second half of the rating. Higher both the digits, better the battery quality.

4.   Cold Cranking Power

This simple rating is applied to all 12-V storage batteries regardless of their size. The battery is loaded at –18°C (0°F) till the total voltage drops to 7.2 V. The output current in amperes is measured for 30 seconds. Higher the output, better the battery.

Example 9.9. *An alkaline cell is discharged at a steady current of 4 A for 12 hours, the average terminals voltage being 1.2 V. To restore it to its original state of charge, a steady current of 3 A for 20 hours is required, the average terminal voltage being 1.44 V. Calculate the ampere-hour (Ah) efficiency and Wh efficiency in this particular case.*

(Principles of Elect. Engg.-I, Jadavpur Univ.)

Solution. As discussed in Art. 9.19

$$\text{Ah efficiency} = \frac{\text{Ah of discharge}}{\text{Ah of charge}} = \frac{12 \times 4}{20 \times 3} = \textbf{0.8} \quad \textbf{or} \quad \textbf{80\%}$$

$$\text{Wh efficiency} = \text{Ah effi.} \times \frac{\text{Av. volts on discharge}}{\text{Av. volts on charge}} = \frac{0.8 \times 1.2}{1.44} = \textbf{0.667} \quad \textbf{or} \quad \textbf{66.7\%}$$

Example 9.10. *A discharged battery is charged at 8 A for 2 hours after which it is discharged through a resistor of R Ω. If discharge period is 6 hours and the terminal voltage remains fixed at 12 V, find the value of R assuming the Ah efficiency of the battery as 80%.*

Solution. Input amp-hours $= 8 \times 2 = 16$
Efficiency $= 0.8$ ∴ Ah output $16 \times 0.8 = 12.8$

Discharge current $= 12.8/6 \text{ A}$ ∴ $R = \dfrac{12}{12.8/6} = \dfrac{6 \times 12}{12.8} = \textbf{5.6 Ω}$

9.22.   Indications of a Full-charged Cell

The indications of a fully-charged cell are :

(*i*)   *gassing* (*ii*) *voltage* (*iii*) *specific gravity and* (*iv*) *colour of the plates.*

(*i*)   **Gassing**

When the cell is fully charged, it freely gives off hydrogen at cathode and oxygen at the anode, the process being known as "Gassing". Gassing at *both* plates indicates that the current is no longer doing any useful work and hence should be stopped. Moreover, when the cell is fully charged, the electrolyte assumes a milky appearance.

(*ii*)   **Voltage**

The voltage ceases to rise when the cell becomes fully-charged. The value of the voltage of a fully-charged cell is a variable quantity being affected by the rate of charging, the temperature and specific gravity of the electrolyte etc. The approximate value of the e.m.f. is 2.1 V or so.

(*iii*)   **Specific Gravity of the Electrolyte**

A third indication of the state of charge of a battery is given by the specific gravity of the electrolyte. We have seen from the chemical equations of Art. 9.9, that during discharging , the density of electrolyte decreases due to other production of water, whereas it increases during charging due to the

absorption of water. The value of density when the cell is fully charged is 1.21 and 1.18 when discharged up to 1.8 V. Specific gravity can be measured with a suitable hydrometer which consists of a float, a chamber for the electrolyte and a squeeze bulb.

(*iv*) Colour

The colour plates, on full charge is deep chocolate brown for positive plate and clear slate gray for negative plate and the cell looks quite brisk and alive.

9.23.   Applications of Lead-acid Batteries

Storage batteries are these days used for a great variety and range of purposes, some of which are summarised below :

1. In Central Stations for supplying the whole load during light load periods, also to assist the generating plant during peak load periods, for providing reserve emergency supply during periods of plant breakdown and finally, to store energy at times when load is light for use at time when load is at its peak value.

2. In private generating plants both for industrial and domestic use, for much the same purpose as in Central Stations.

3. In sub-stations, they assist in maintaining the declared voltage by meeting a part of the demand and so reducing the load on and the voltage drop in, the feeder during peak-load periods.

4. As a power source for industrial and mining battery locomotives and for road vehicles like cars and trucks.

5. As a power source for submarines when submerged.

6. Marine applications include emergency or stand-by duties in case of failure of ship's electric supply, normal operations where batteries are subjected to regular cycles of charge and discharge and for supplying low-voltage current to bells, telephones, indicators and warning systems etc.

7. For petrol motor-car starting and ignition etc.

8. As a low voltage supply for operating purposes in many different ways such as high-tension switchgear, automatic telephone exchange and repeater stations, broadcasting stations and for wireless receiving sets.

9.24.   Voltage Regulators

As explained in Art. 9.20, the voltage of a battery varies over a considerable range while under discharge. Hence, it is necessary to find some means to control the battery voltage upto the end so as to confine variations within reasonable limits – these limits being supplied by the battery.

Fig. 9.15

The voltage control systems may be hand-operated or automatic. The simplest form of hand-operated control consists of a rheostat having a sufficient number of steps so that assistance can be inserted in the circuit when battery is fully charged and gradually cut out as the discharge continues, as shown in Fig. 9.15.

The above system can be designed for automatic operation as shown in Fig. 9.16. A rise in voltage results in the release of pressure on the carbon block rheostat, thereby increasing its resistance whereas a fall in voltage results in increasing the pressure on the block thereby decreasing its resistance. By this automatic variation of control resistance, variations in battery voltage are automatically controlled.

Fig. 9.16

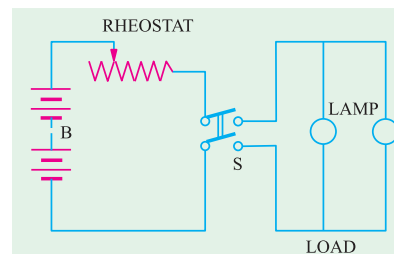## 9.25.   End-cell Control System

The use of rheostat for controlling the battery

Fig. 9.17

voltage is objectionable especially in large-capacity installations where the I^2R loss would be considerable. Hence other more economical systems have been developed and put into use. One such system is the end-cell control system. It consists of suitable regulator switches which cut one or more of a selected number of cells out of the circuit when the battery is fully charged and into the circuit again as the discharge continues. To make the process of cutting cells in and out at the battery circuit simple, the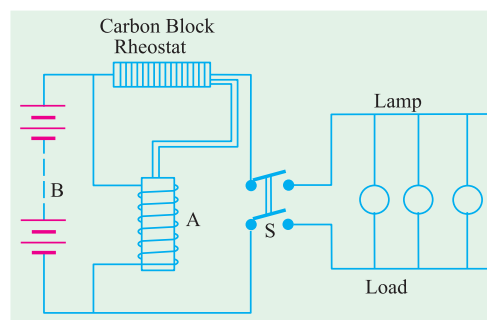 group of 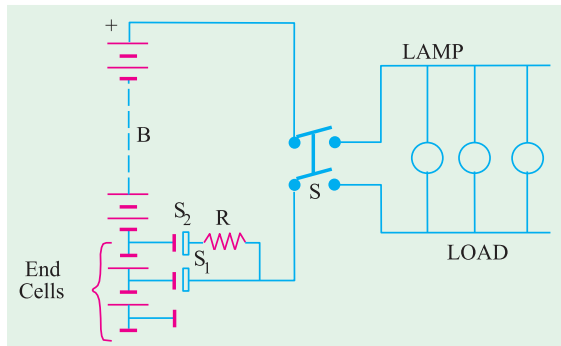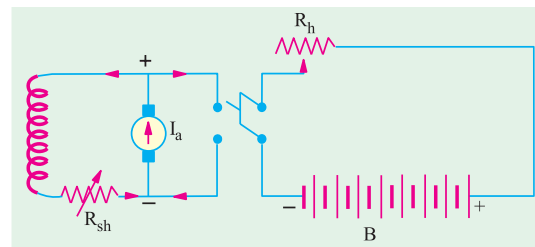cells selected for this control is situated at one end of the battery where from it derives the name *end cell.* By moving the contact arm of the switch to the left or right, cells are cut in or out of the discharge circuit and so the voltage is varied accordingly.

For making the end-cell switch operate without opening the circuit or shortcircuiting the cells during its passage from one cell to another, an auxiliary constraint S_2 is employed. S_2 prevents the circuit from being open entirely but has sufficient resistance R between it and the main contact arm S_1 to prevent any objectionably large current to flow on short-circuit. The above mechanism usually incorporates devices for preventing the stoppage of the switch in the short-circuit position.

9.26. Number of End-cells

For maintaining a supply voltage of V volts from a battery of lead-acid cells when the latter are approaching their discharge voltage of 1.83 (depending on the discharge rate), the number of cells required is $V/1.83$. When the battery is fully charged with each cell having an e.m.f. of 2.1 V, then the number of cells required is $V/2.1$. Hence, the number of end-cells required is $(V/1.83 - V/2.1)$. These are connected to a regulating switch which adds them in series with the battery one or two at a time, as the discharge proceeds.

9.27. Charging Systems

In various installations, batteries are kept floating on the line and are so connected that they are being charged when load demands are light and automatically discharged during peak periods when load demands are heavy or when the usual power supply fails or is disconnected. In some other installations, the battery is connected to the feeder circuit as and when desired, allowed to discharge to a certain point, then removed and re-charged for further requirements.

For batteries other than the 'floating' and 'system-governed' type, following two general methods (though there are some variations of these) are employed.

    (*i*) *The Constant-current System* and (*ii*) *The Constant-voltage System.*

9.28. Constant-current System

In this method, the charging current is kept constant by varying the supply voltage to overcome the increased back e.m.f. of cells. If a charging booster (which is just a shunt dynamo directly driven by a motor) is used, the current supplied by it can be kept constant by adjusting its excitations. If charged on a d.c. supply, the current is controlled by varying the rheostat con-

Fig. 9.18

nected in the circuit. The value of charging current should be so chosen that there would be no

excessive gassing during final stages of charging and, also, the cell temperature does not exceed 45°C. This method takes a comparatively longer time.

9.29. Constant-voltage System

In this method, the voltage is kept constant but it results in very large charging current in the beginning when the back e.m.f. of the cells is low and a small current when their back e.m.f. increases on being charged.

With this method, time of charging is almost reduced to half. It increases the capacity by approximately 20% but reduces the efficiency by 10% or so.

Calculations

When a secondary cell or a battery of such cells is being charged, then the emf of the cells acts in opposition to the applied voltage. If V is the supply voltage which sends a charging current of I against the back e.m.f. E_b, then input is VI but the power spent in overcoming the opposition (Fig. 9.19) is $E_b I$. This power $E_b I$ is converted into the chemical energy which is stored in the cell. The charging current can be found from the following equation :
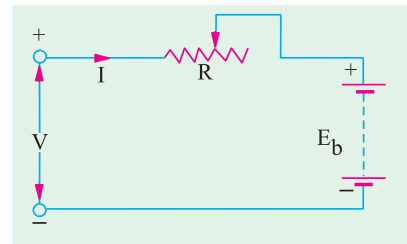

Fig. 9.19

$$I = \frac{V - E_b}{R}$$

where R = total circuit resistance including internal resistance of the battery

              I = charging current

By varying R, the charging current can be kept constant throughout.

Example 9.11. *A battery of accumulators of e.m.f. 50 volt and internal resistance 2 Ω is charged on 100 volt direct means. What series resistance will be required to give a charging current of 2 A?*

If the price of energy is 50 paise per kWh, what will it cost to charge the battery for 8 hours and what percentage of energy supplied will be used in the form of heat ?

Solution. Applied voltage   = 100 V; Back e.m.f. of the battery = 50 V

Net charging voltage   = 100 −50 = 50 V

Let R be the required resistance, then 2 = 50/(R + 2); R = 46/2 = 23 Ω

Input for eight hours   = 100 × 2 × 8 = 1600 Wh = 1.6 kWh

Cost = 50 × 1.5 = **80 paise;** Power wasted on total resistance = $25 \times 2^2 = 100$ W

Total input = 100 × 2 = 200 W : Percentage waste = 100 × 100/200 = **50 %**

Example 9.12. *A 6-cell, 12-V battery is to be charged at a constant rate of 10 A from a 24-V d.c. supply. If the e.m.f. of each cell at the beginning and end of the charge is 1.9 V and 2.4 V, what should be the value of maximum resistance to be connected in series with the battery. Resistance of the battery is negligible.*

Solution. Beginning of Charging

Total back e.m.f. of battery   = 6 × 1.9 = 11.4 volt

Net driving voltage   = 24 −11.4 = 12.6 V ; R_{max} = 12.6/10 = **1.26 Ω**

End of Charging

Back e.m.f. of battery   = 6 × 2.4 = 14.4 volt

Net driving voltage   = 24 −14.4 = 9.6 V; R_{min} = 9.6/10 = **0.96 Ω**

Example 9. 13. *Thirty accumulators have to be charged from their initial voltage of 1.8 V using a direct current supply of 36 volt. Each cell has an internal resistance of 0.02 Ω and can be charged at 5 amperes. Sketch a circuit by which this can be done, calculating the value of any resistance or resistances used. What will be the current taken from the mains towards the end of the charging period when the voltage has risen to 2.1 volt per cell ?*

Solution. Since the supply voltage (36 V) is less than the back e.m.f. of the 30 cell battery (54 V), hence the cells are divided into two equal groups and placed in parallel across the supply for charging as shown in Fig. 9.20. It would be economical to use a separate resistance R in series with each group.

Here $V = 36$ V, $E_b = 15 \times 1.8 = 27$ V

Internal resistance of each parallel group

$$= 15 \times 0.02 = 0.3 \; \Omega$$

Charging current = 5A ∴ $5 = \dfrac{36-27}{R+0.3}$

$$R = \textbf{1.5 } \boldsymbol{\Omega}$$

Now, when the voltage per cell becomes 2.1 V, then back e.m.f. of each parallel group = $15 \times 2.1 = 31.5$ V

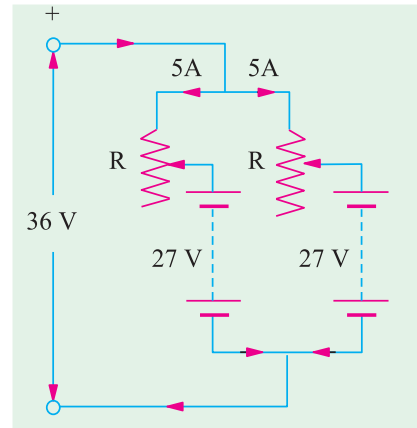∴   Charging current $= \dfrac{36-31.5}{1.5+0.3} = \textbf{2.5 A}$

Fig. 9.20

Example 9.14. *A battery of 60 cells is charged from a supply of 250 V. Each cell has an e.m.f. of 2 volts at the start of charge and 2.5 V at the end. If internal resistance of each cell is 0.1 Ω and if there is an external resistance of 19 Ω in the circuit, calculate (a) the initial charging current (b) the final charging current and (c) the additional resistance which must be added to give a finishing charge of 2 A rate.*

Solution. (*a*) Supply voltage $V = 250$ V

Back e.m.f. of the battery E_b at start = $60 \times 2 = 120$ V and at the end = $60 \times 2.5 = 150$ V

Internal resistance of the battery $= 60 \times 0.1 = 6 \; \Omega$

Total circuit resistance $= 19 + 6 = 25 \; \Omega$

(*a*) Net charging voltage at start $= 250 - 120 = 130$ V

∴   Initial charging current $= 130/25 = \textbf{5.2 A}$

(*b*) Final charging current $= 100/25 = \textbf{4 A}$

(*c*) Let R be the external resistance, then

$2 = \dfrac{100}{R+6}$ ∴ $R = 88/2 = 44 \; \Omega$

∴   Additional resistance required = $44 - 19 = \textbf{25 } \boldsymbol{\Omega}$

Fig. 9.21

Example 9.15. *Two hundred and twenty lamps of 100 W each are to be run on a battery supply at 110 V. The cells of the battery when fully charged have an e.m.f. of 2.1 V each and when discharged 1.83 V each. If the internal resistance per cell is 0.00015 Ω (i) find the number of cells in the battery and (ii) the number of end cells. Take the resistance of the connecting wires as 0.005 Ω*

Solution. Current drawn by lamps = $220 \times 100/110 = 200$ A

Voltage drop on the resistance of the connecting wires = $0.005 \times 200 = 1.0$ V
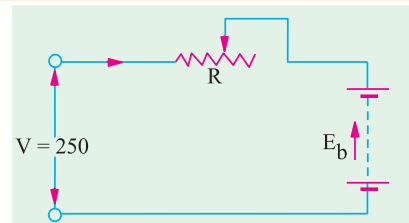
Battery supply voltage = $110 + 1 = 111$ V

Terminal voltage/cell when fully charged and supplying the load

$$= 2.1 - (200 \times 0.00015) = 2.08 \text{ V}$$

Terminal voltage/cell when discharged

$$= 1.83 - (200 \times 0.00015) = 1.8 \text{ V}$$

(*i*) No. of cells in the battery = 111/2.08

$$= 53.4 \text{ say, } \textbf{54}$$

(*ii*) No. of cells required when discharged

$$= 111/1.8 = 62$$

Hence, number of end cells = 62 − 54 = **8**
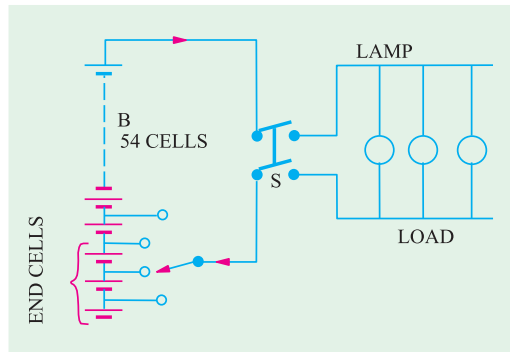
The connections are shown in Fig. 9.22.

Fig. 9.22

Example 9.16. *A storage battery consists of 55 series-connected cells each of internal resistance 0.001 Ω and e.m.f. 2.1 V. Each cell consists of 21 plates, ten positive and eleven negative, each plate measuring 20 × 25 cm. If full-load current per cell is 0.01 A per cm² of positive plate surface, find (i) full-load terminal voltage of the battery and (ii) power wasted in the battery if the connectors have a total resistance of 0.025 Ω.*

Solution. Since both sides of a positive plate are utilized, the area of both sides will be taken into consideration.

Total area (both sides) of ten positive plates = $2 \times 20 \times 25 \times 10 = 10,000 \text{ cm}^2$

Full load current = $10,000 \times 0.01 = 100 \text{ A}$

Voltage drop in battery and across connectors = $100 [(55 \times 0.001) + 0.025] = 8 \text{ V}$

Battery e.m.f. = $55 \times 1.2 = 115.5 \text{ V}$

(*i*) Battery terminal voltage on full-load = $115.5 - 8 = \textbf{107.5 V}$

(*ii*) Total resistance = $(55 \times 0.001) + 0.025 = 0.08 \text{ Ω}$; Power loss = $100^2 \times 0.08 = \textbf{800 W.}$

Example 9.17. *A charging booster (shunt generator) is to charge a storage battery of 100 cells each of internal resistance 0.001 Ω. Terminal p.d. of each cell at completion of charge is 2.55 V. Calculate the e.m.f. which the booster must generate to give a charging current of 20 A at the end of charge. The armature and shunt field resistances of the generator are 0.2 and 258 Ω respectively and the resistance of the cable connectors is 0.05 Ω.*

Solution. Terminal p.d. per cell = 2.55 volt

The charging voltage across the battery must be capable of overcoming the back e.m.f. and also to supply the voltage drop across the internal resistance of the battery.

Back e.m.f. = $100 \times 2.55 = 255 \text{ V}$

Voltage drop on internal resistance

$$= 100 \times 0.001 \times 20 = 2 \text{ V}$$

∴ P.D. across points *A* and *B* = 255 + 2 = 257 V

P.D. across terminals *C* and *D* of the generator

$$= 257 + (20 \times 0.05) = 258 \text{ V}$$

Fig. 9.23

∴ $I_{sh} = 258/258 = 1\text{A}; \; I_a = 20 + 1 = 21 \text{ A}$

∴ $I_a R_a = 21 \times 0.2 = 4.2 \text{ V}$

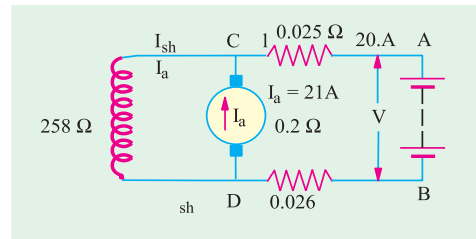∴ Generated e.m.f. $= 258 + 4.2 = \textbf{262.2 V}$

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Tutorial Problems No. 9.2

1. A 60-cell storage battery having a capacity of 360 Ah takes 8 hours when charged by a dc generator at a voltage of 220 V. Calculate the charging current and the range of the rheostat required to ensure a constant charging current. The emf of each cell is 1.8 V at the beginning of charging and 2.7 V at the end of the charging. Ignore the internal resistance of the cell.

[45 A; 2.45 to 1.29 Ω]

2. A storage battery consists of 55 series connected cells each of internal resistance 0.001 Ω and e.m.f. 2.1 V. Each cell consists of 21 plates, ten positive and eleven negative, each plate measuring 20×25 cm. If full-load current per cell is 0.01 A per cm^2 of positive plate surface, find (*i*) full-load terminal voltage of the battery and (*ii*) power wasted in the battery if the connectors have a total resistance of 0.025 Ω

[(*i*) 107.5 V (*ii*) 800 W]

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9.30. Trickle Charging

When a storage battery is kept entirely as an emergency reserve, it is very essential that it should be found fully charged and ready for service when an emergency arises. Due to leakage action and other open-circuit losses, the battery deteriorates even when idle or on open-circuit. Hence, to keep it fresh, the battery is kept on a trickle charge. The rate of trickle charge is small and is just sufficient to balance the open-circuit losses. For example, a standby battery for station bus-bars capable of giving 2000 A for 1 hour or 400 Ah at the 10-hr rate, will be having a normal charging rate of 555 A, but a continuous 'trickle' charge of 1 A or so will keep the cells fully charged (without any gassing) and in perfect condition. When during an emergency, the battery gets discharged, it is recharged at its normal charging rate and then is kept on a continuous trickle charge.

9.31. Sulphation-Causes and Cure

If a cell is left incompletely charged or is not fully charged periodically, then the lead sulphate formed during discharge, is not converted back into PbO_2 and Pb. Some of the unreduced $PbSO_4$ which is left, gets deposited on the plates which are then said to be sulphated. $PbSO_4$ is in the form of minute crystals which gradually increase in size if not reduced by thoroughly charging the cells. It increases the internal resistance of the cell thereby reducing its efficiency and capacity. Sulphation also sets in if the battery is overcharged or left discharged for a long time.

Sulphated cells can be cured by giving them successive overcharges, for which purpose they are cut out of the battery during discharge, so that they can get two charges with no intervening discharge. The other method, in which sulphated cells need not be cut out of the battery, is to continue charging them with a '*milking booster*' even after the battery as a whole has been charged. A milking booster is a motor-driven low-voltage dynamo which can be connected directly across the terminals of the sulphated cells.

9.32. Maintenance of Lead-acid Cells

The following important points should be kept in mind for keeping the battery in good condition:

1. Discharging should not be prolonged after the minimum value of the voltage for the particular rate of discharge is reached.
2. It should not be left in discharged condition for long.
3. The level of the electrolyte should always be 10 to 15 mm above the top of the plates which must not be left exposed to air. Evaporation of electrolyte should be made up by adding distilled water occasionally.
4. Since acid does not vaporise, none should be added.

5. Vent openings in the filling plug should be kept open to prevent gases formed within from building a high pressure.
6. The acid and corrosion on the battery top should be washed off with a cloth moistened with baking soda or ammonia and water.
7. The battery terminals and metal supports should be cleaned down to bare metal and covered with vaseline or petroleum jelly.

9.33. Main Operated Battery Chargers

A battery charger is an electrical device that is used for putting energy into a battery. The battery charger changes the a.c. from the power line into d.c. suitable for charger. However, d.c. generator and alternators are also used as charging sources for secondary batteries.

In general, a mains-operated battery charger consists of the following elements :

1. A step-down transformer for reducing the high a.c. mains voltage to a low a.c. voltage.

2. A half-wave or full-wave rectifier for converting alternating current into direct current.

3. A charger-current limiting element for preventing the flow of excessive charging current into the battery under charge.

4. A device for preventing the reversal of current *i.e.* discharging of the battery through the charging source when the source voltage happens to fall below the battery voltage.

In addition to the above, a battery charger may also have circuitry to monitor the battery voltage and automatically adjust the charging current. It may also terminate the charging process when the battery becomes fully charged. However, in many cases, the charging process is not totally terminated but only the charging rate is reduced so as to keep the battery on trickle charging. These requirements have been illustrated in Fig. 9.24.

Most of the modern battery chargers are fully protected against the following eventualities :
(*a*) They are able to operate into a short-circuit.
(*b*) They are not damaged by a reverse-connected battery.
(*c*) They are operated into a totally flat battery.
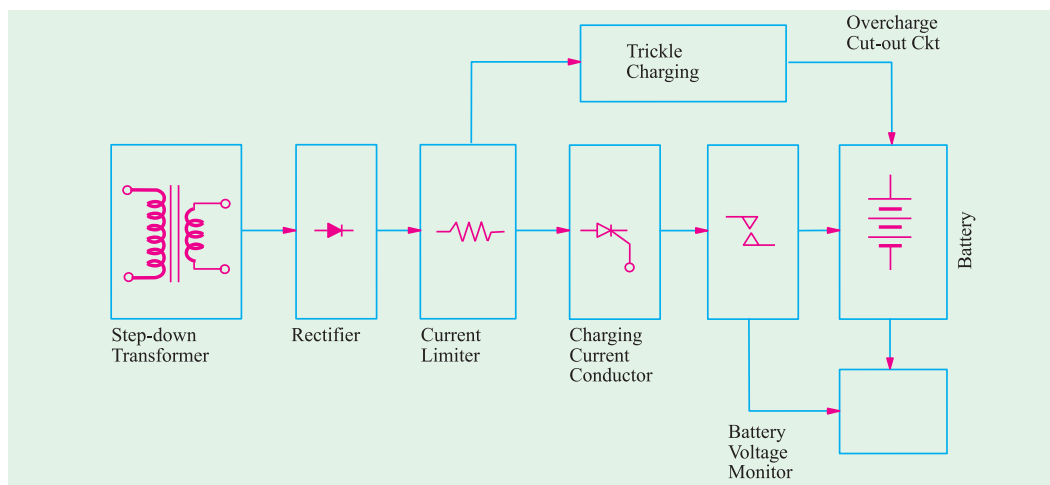(*d*) They can be regulated both for current and voltage.

Fig. 9.24

9.34. Car Battery Charger Using SCR

Fig. 9.25 shows the circuitry of a very simple lead-acid battery charger which has been provided

protection from load short-circuit and from reverse battery polarity. The *SCR* is used as a half-wave rectifier as well as switching element to terminate the high-current charging process when battery gets fully-charged.

Working

The *SCR* acts as a half-wave rectifier during only the positive half-cycles of the secondary voltage when point *M* in Fig. 9.25 is at a positive potential. The *SCR* does not conduct during the negative half-cycle of the secondary voltage when point *M* achieves negative potential. When *M* is at positive potential, the *SCR* is triggered into conduction because of the small gate current I_g passing via R_1 and diode D_1. In this way, the charging current *I* after passing through R_5 enters the battery which is being charged.

In the initial state, when the battery voltge is low, the potential of point *A* is also low (remember that R_3, R_4 and preset resistor R_6 are connected across the battery via R_5) which means that the forward bias on the base of transistor *T* is not sufficient to make it conduct and thereby stop the conduction of *SCR*. Hence, *SCR* keeps conducting , consequently, keeps charging the battery through the current limiting resistor R_5.
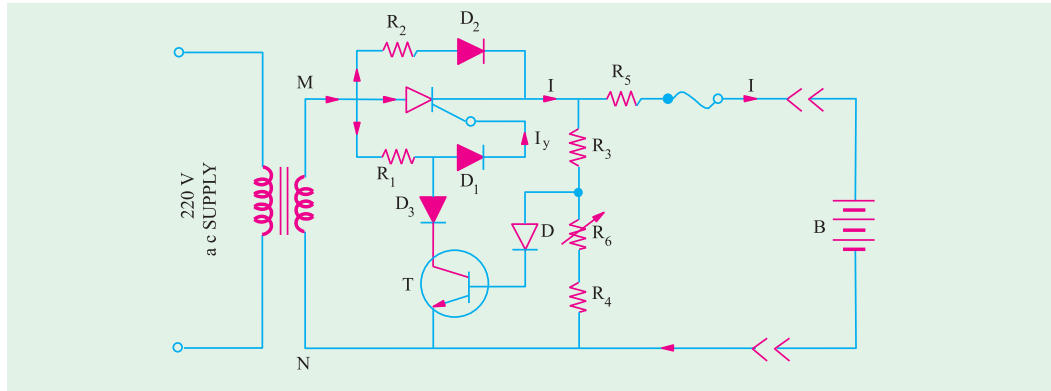

Fig. 9.25

As the battery gets progressively charged, its voltage rises and when it becomes fully charged, the potential of point *A* increases thereby increasing the forward bias of *T* which starts conducting. In that case, *T* bypasses the triggering gate current of the *SCR* via R_1 and D_3. Since the *SCR* can no longer be triggered, the charging process stops. However, a small trickle charging current keeps flowing via. R_2 and D_2. The function of diode D_2 is to prevent reverse flow of the current through the battery when point *M* has negative potential during the negative cycle of the secondary voltage. The value of trickle charging current is determined by R_2 because R_5 has a fixed but small value. The resistor R_5 also limits the flow of excessive charging current when the charger is connected to a completely dead battery.

The charger described above is not suitable for fast charging because it utilizes half-wave rectification. Most of the mains-operated chargers working on a single-phase supply use a full-wave rectifier consisting of a center-tapped tarnsformer and two diodes or a bridge circuit using for diodes.

9.35. Automobile Battery Charger Using Full-wave Rectifier

The battery charger shown in Fig. 9.26, is used to recharge run-down lead-acid batteries in automobiles without removing them from their original mountings and without any need for constant attention. When the battery is fully charged, the circuit automatically switches from charging current to trickle charging and an indicator lamp lights up to provide a visual indication of this condition.

As shown in Fig. 9.26, diodes D_1, and D_2 form a full-wave rectifier to provide pulsating direct current for charging the battery. The battery is charged through the *SCR* which is also used as switch to terminate the charging process when the battery becomes fully charged. The two transistors T_1 and T_2 together form an electronic switch that has two stable states *i.e.* the *ON* state in which T_1 and T_2 conduct and the OFF state in which T_1 and T_2 do not conduct. The ON-OFF state of this switch is decided by the battery voltage and setting of the "current adjust" potentiometer R_6.
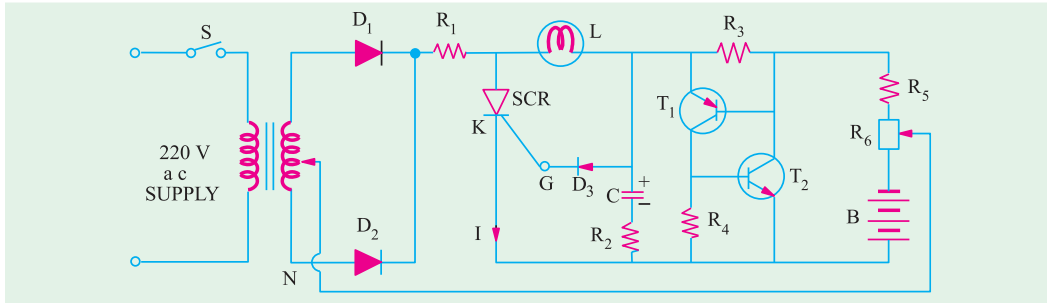

Fig. 9.26

Working

When switch S is turned on, the full-wave rectified output of D_1 and D_2 charges capacitor C through R_1, lamp L and R_2. In a very short time, capacitor voltage rises high enough to make diode D_3 conduct the gate current thereby triggering *SCR* into conduction during each half-cycle of the output voltage. Hence, full charging current is passed through the cathode K of the *SCR* to the positive terminal of the battery whose negative terminal is connected directly to the center tap of the step-down transformer. Resistor R_1 limits the charging current to a safe value in order to protect the rectifier diodes D_1 and D_2 in case the load happens to be a "dead" battery.

When the battery is being charged and has low voltage, the two transistors T_1 and T_2 remain in the non-conducting state. However, when the battery voltage rises and finally the battery becomes fully-charged, the two transistors T_1 and T_2 (which form a regenerative switch) are triggered into conduction at a point set by R_6. In this way, T_1 and T_2 provide a low-impedance discharge path for C. Hence, C discharges through R_2 and the $T_1 - T_2$ switch, thereby cutting off the gate current of the *SCR* which stops conducting thereby terminating the battery charge. Thereafter, small trickle charge current keeps on flowing into the battery via L and the regenerative switch formed by T_1 and T_2. A glowing lamp L indicates that the battery is under trickle charging.

Fig. 9.27 shows the same circuit as shown in Fig. 9.26 except that the two-diode full-wave rectifier has been replaced by a full-wave bridge rectifier using four diodes.
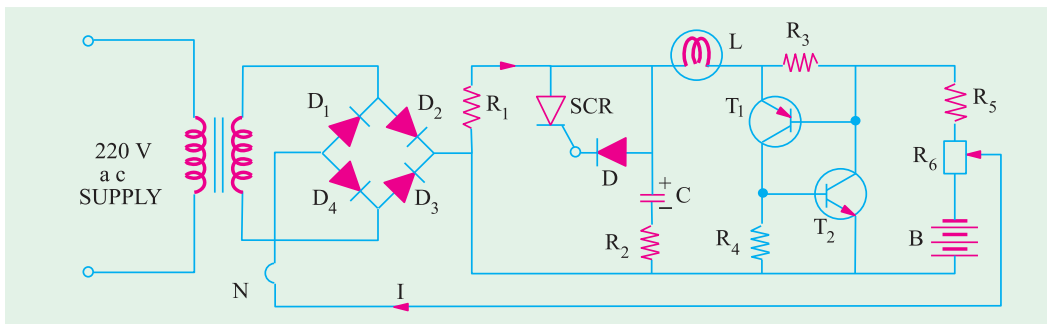

Fig. 9.27

9.36. Static Uninterruptable Power Systems (UPS)

The function of a *UPS* is to ensure absolute continuity of power to the computerised control systems thereby protecting critical equipment from electrical supply failure. A *UPS* makes it possible to provide a 'clean' reliable supply of alternating current free of sags of surges in the line voltage, frequency variation, spikes and transients. *UPS* systems achieve this by rectifying the standard mains supply, using the direct current to charge the standby battery and to produce 'clean' alternating current by passing through an inverter and filter system.

Components of a *UPS* System

The essential components of a *UPS* system as shown in Fig. 9.28 are as under :

1. A rectifier and thyristor-controlled battery charger which converts the *AC* input into regulated *DC* output and keeps the standby battery fully charged.
2. A standby battery which provides *DC* input power to inverter during voltage drops or on failure of the normal mains *AC* supply.
3. An inverter which converts *DC* to clean *AC* thus providing precisely regulated output voltage and frequency to the load as shown.

Working

As shown in Fig. 9.28 the main flow of energy is from the rectifier to the inverter with the standby battery kept on 'float'. If the supply voltage falls below a certain level or fails completely, the battery output to the inverter maintains a clean a.c. supply. When the mains power supply is resorted, the main energy flow against starts from the rectifier to the inverter but, in addition, the rectifier recharges the battery. When the standby battery gets fully charged, the charging current is automatically throttled back due to steep rise in the back e.m.f. of the battery . An automatic/manual bypass switch is used to connect the load either directly to the mains a.c. supply or to the inverter a.c. supply.
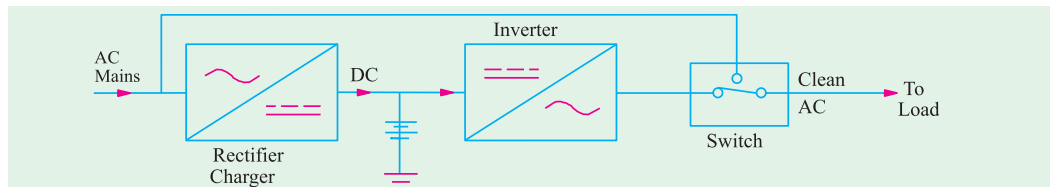

Fig. 9.28

Depending on the application, the voltage of the *UPS* standby battteries may be anywhere between 12 V and 400 V. Typical values are 24 V, 48 V, 110 V and 220 V with currents ranging from a few amperes to 2000 A. Fig. 9.28 shows Everon 4-kVA on-line *UPS* system which works on 170 V-270 V a.c. input and provides an a.c. output voltage of 230 V at 50 Hz frequency with a voltage stability of $\pm$ 2% and frequency stability of $\pm$ 1%. It has zero change over time and has audio beeper which indicates mains fail and battery discharge. It provides 100% protection against line noise, spikes, surges and radio frequency interference. It is manufactured by Everon Electro Systems Pvt. Ltd. New Delhi.

9.37. Alkaline Batteries

Such batteries are ideally suited for portable work. Like lead-acid cells, the alkaline cells also consist of positive and negative plates immersed in an electrolyte. The plates and the electrolyte are placed in a suitable-container.

The two types of alkaline batteries which are in general use are :

(*i*) nickel-iron type of Edison type.

(*ii*) nickel-cadmium type of Jungnor type which is commercially known as NIFE battery.
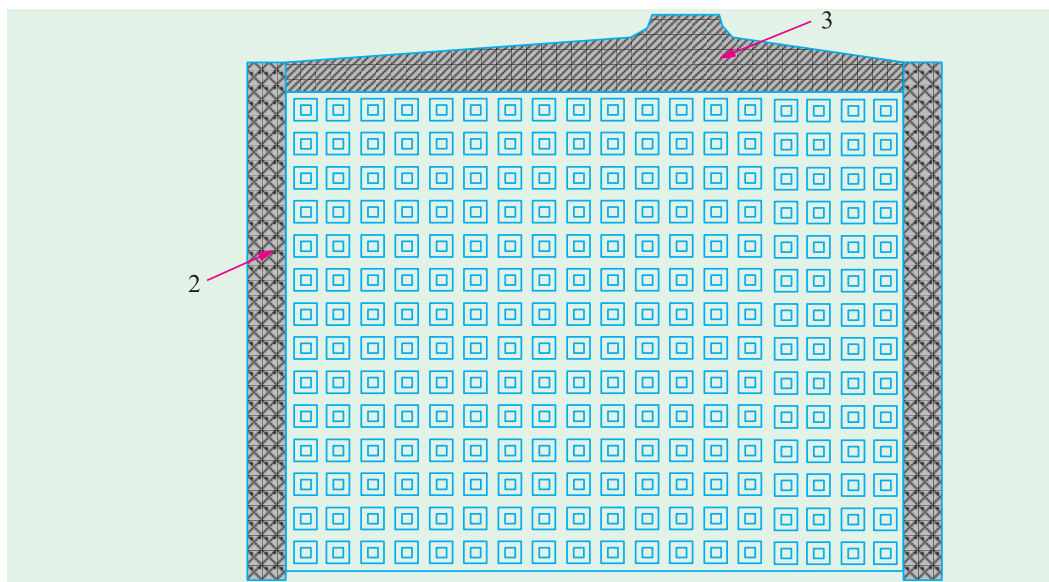
Fig. 9.29

Another alkaline battery which differs from the above only in the mechanical details of its plates is known as Alkum battery which uses nickel hydroxide and graphite in the positive plates and a powdered alloy of iron and chromium in the negative plates.

Silver-zinc type of alkaline batteries are also made whose active material for the positive plate is silver oxide (Ag_2O) and for negative plate is zinc oxide and zinc powder. The electrodes or plates of the alkaline cells are designed to be either of the enclosed-pocket type or open-pocket type. In the case of enclosed-pocket type plates, the active material is inside perforated metal envelopes whereas in the other type, the active material is outside directly in contact with the electrolyte. As shown in Fig. 9.29, the active material of the enclosed-pocket type plates is enclosed in nickel-plated perforated steel pockets or packs which are pressed into the steel frames of the plates.

The open-pocket type plates are made of the following three materials :

(i) metal-ceramic plate-the frame of the plate is a nickel-plated steel grid with the active material pressed in under a pressure of 800 to 1900 kg/cm^2.

(ii) foil plate-the base of such a plate is a thin nickel foil coated with a layer of nickel suspension deposited by a spray technique.

(iii) pressed plates–the base member of these plates is a nickel–plated pressed steel grid. The active material is pressed into them at a pressure of about 400 kg/cm^2.

9.38. Nickel-iron and Edison Batteries

There is revived interest in the nickel-iron battery because it seems to be one of the few systems which may be developed into a high-energy density battery for electric vehicles. Since long the two main designs for this battery have been the tubular positive type and the flat pocket plate type although cells with sintered type negative are also being manufactured.

The active materials in a nickel-iron cell are :

(i) Nickel hydroxide $Ni(OH)_4$ or apple green nickel peroxide NiO_2 for the positive plate. About 17 per cent of graphite is added to increase conductivity. It also contains an activating additive barium hydroxide which is about 2 per cent of the active material. This additive increases the service life of the plates.
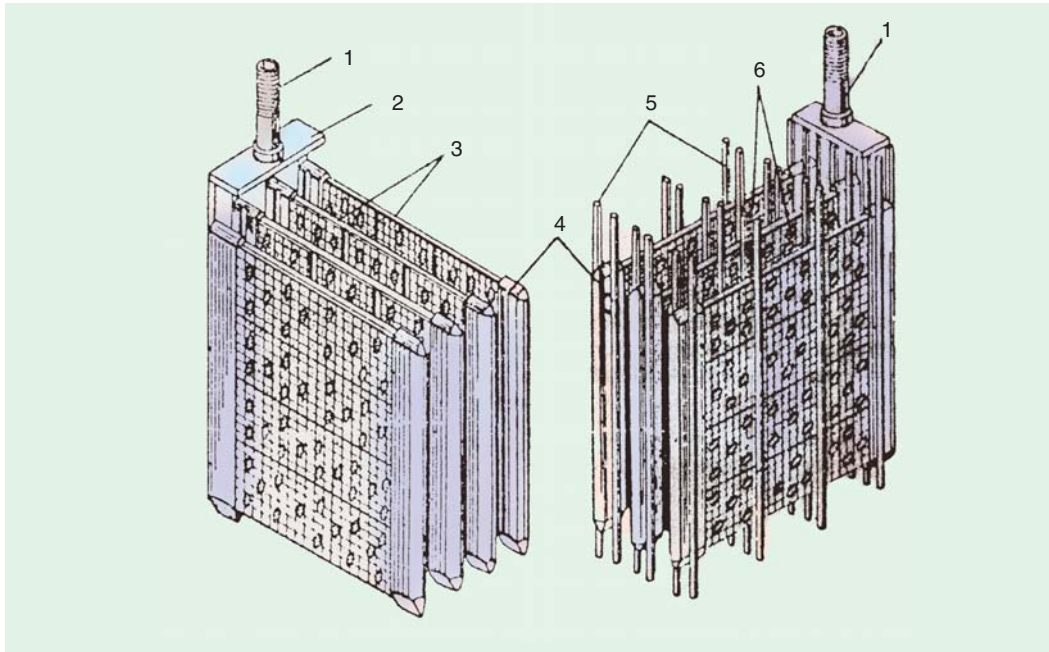
Fig. 9.30 Plates groups of an alkaline cell

(*a*) + ve group (*b*) – ve group, 1–terminal post 2–connecting strap, 3–plates.
4–plates side members. 5–ebonite spacer sticks. 6–pockets.

(***ii***) powdered iron and its oxides for the negative plate. Small quantities of nickel sulphate and ferrous sulphide are added to improve the performance of the coil.

(***iii***) the electrolyte is 21 per cent solution of caustic potash KOH (potassium hydrate) to which is added a small quantity of lithium hydrate LiOH for increasing the capacity of the cell.

As shown in Fig. 9.30, plates of the same polarity with their pockets filled, are assembled into cells groups for which purpose they are welded to a common strap having a threaded post.

The number of negative plates is one more than the positive plates. The extreme negative plates are electrically connected to the container. Ebonite separating sticks are placed between the positive and negative plates to prevent any short-circuiting.
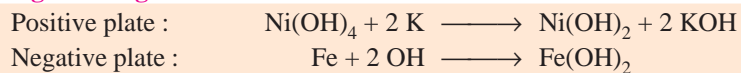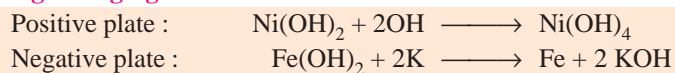
The steel containers of the batteries are press-formed from steel and the joints are welded. The body and the cover are nickel-plated and have a dull finish. However, it should be kept in mind that since these containers are electrically alive, no loose wires should touch them owing to the danger of severe sparking from short-circuits.

9.39. Chemical Changes

The exact nature of the chemical changes taken place in such a cell is not clearly understood because the exact formula for the nickel oxide is not yet well established but the action of the cell can be understood by assuming the peroxide NiO_2 or its hydrated form $Ni(OH)_4$.

First, let us assume that at positive plate, nickel oxide is in its hydrate form $Ni(OH)_4$. During discharge, electrolyte KOH splits up into positive K ions and negative OH ions. The K ions go to anode and reduce $Ni(OH)_4$ to $NI(OH)_2$. The OH ions travel towards the cathode and oxidise iron. During charging, just the opposite reactions take place *i.e.* K ions go to cathode and OH ions go to anode. The chemical reactions can be written thus :

$$KOH \longrightarrow K + OH$$

During discharge

Positive plate : $\qquad$ $Ni(OH)_4 + 2 K \longrightarrow Ni(OH)_2 + 2 KOH$

Negative plate : $\qquad$ $Fe + 2 OH \longrightarrow Fe(OH)_2$

During Charging

Positive plate : $\qquad$ $Ni(OH)_2 + 2OH \longrightarrow Ni(OH)_4$

Negative plate : $\qquad$ $Fe(OH)_2 + 2K \longrightarrow Fe + 2 KOH$

The charging and discharging can be represented by a single reversible equation thus :

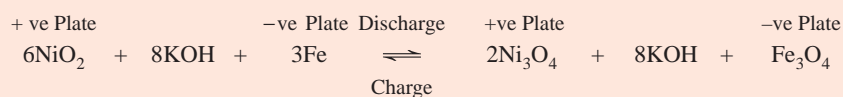$$\underset{\text{Pos. Plate}}{Ni(OH)_4} + \underset{\text{Neg. Plate}}{KOH} + Fe \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} \underset{\text{Pos. Plate}}{Ni(OH)_2} + KOH + \underset{\text{Neg. Plate}}{Fe(OH)_2}$$
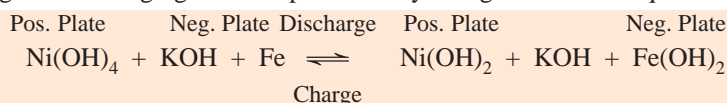
It will be observed from the above equation that as no water is formed, there is no overall change in the strength of the electrolyte. Its function is merely to serve as a conductor of as a vehicle for the transfer of OH ions from one plate to another. Hence, the specific gravity of the electrolyte remains practically constant, both during charging and discharging. That is why only a small amount of electrolyte is required which fact enables the cells to be small in bulk.

Note. If, however, we assume the nickel oxide to be in the form NiO_2, then the above reactions can be represented by the following reversible equation :

$$\underset{\text{+ ve Plate}}{6NiO_2} + 8KOH + \underset{\text{−ve Plate}}{3Fe} \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} \underset{\text{+ve Plate}}{2Ni_3O_4} + 8KOH + \underset{\text{−ve Plate}}{Fe_3O_4}$$

9.40. Electrical Characteristics

The e.m.f. of an Edison cell, when fully charged, is nearly 1.4 V which decreases rapidly to 1.3 V and then try slowly on 1.1 or 1.0 V on discharge. The average discharge voltage for a 5-hour discharge rate is 1.2 V. Hence, for the same average value of the voltage, an alkali accumulator will consist of 1.6 to 1.7 times as many cells as in a lead-acid battery. Internal resistance of an alkali cell is nearly five times that of the lead-acid cell, hence there is a relatively greater difference between its terminal voltage when charging and discharging.

The average charging voltage for an alkali cell is about 1.7 V. The general shapes of the charge and discharge curves for such cells are, however, similar to those for lead-acid cells. The rated capacity of nickel accumulators usually refers to either 5-hour or 8-hour discharge rate unless stated otherwise.

The plates of such cells have greater mechanical strength because of all-steel construction. They are comparatively lighter because (*i*) their plates are lighter and (*ii*) they require less quantity of electrolyte. They can withstand heavy charge and discharge currents and do not deteriorate even if left discharged for long periods.

Due to its relatively higher internal resistance, the efficiencies of an Edison cell are power than those of the lead acid cell. On the average, its Ah efficiency is about 80% and Wh efficiency 60 or 50%. It has an average density of 50 Wh/kg.

With increase in temperature, e.m.f. is increased slightly but capacity increases by an appreciable amount. With decrease in temperature, the capacity decreases becoming practically zero at 4°C even through the cell is fully charged. This is serious drawback in the back in the case of electrically driven vehicles in cold weather and previous have to be taken to heat up the battery before starting, though, in practice, the $I^2 R$ loss in the internal resistance of the battery is sufficient to keep the battery cells warm when running.

The principal disadvantage of the Edison battery on nickel-iron battery is its high initial cost (which will probably be sufficiently reduced when patents expire). At present, an Edison battery costs approximately twice as much as a lead-acid battery designed for similar service. But since the alkaline battery outlasts an indeterminate number of lead-acid batteries, it is cheaper in the end.

Because of their lightness, compact construction, increased mechanical strength, ability to withstand rapid charging and discharging without injury and freedom from corrosive liquids and fumes, alkaline batteries are ideally suited for traction work such as propulsion of electric factory trucks, mine locomotives, miner's lamps, lighting and starting of public service vehicles and other services involving rough usage etc.

9.41. Nickel-Cadmium Batteries

The reactive materials in a nickel-cadmium cell (Fig. 9.31) are :

(*i*) $Ni(OH)_4$ for the positive plate exactly as in the nickel-iron cell.

(*ii*) a mixture of cadmium or cadmium oxide and iron mass to which is added about 3 per cent of solar oil for stabilizing the electrode capacity. The use of cadmium results in reduced internal resistance of the cell.

(*iii*) the electrolyte is the same as in the nickel-iron cell.

The cell grouping and plate arrangement is identical with nickel-iron batteries except that the number of positive plates is more than the negative plates. Such batteries are more suitable than nickel-iron batteries for floating duties in conjunction with a charging dynamo because, in their case, the difference between charging and discharging e.m.f.s is not as great as in nickel-iron batteries.

Nickel-cadmium sintered plate batteries were first manufactured by Germans for military aircrafts and rockets. Presently, they are available in a variety of designs and sizes and have energy density going upto 55 Wh/kg. Their capacity is less affected by high discharge rates and low operating temperature than any other rechargeable batteries. Since such batteries have very low open-circuit losses, they

Fig. 9.31. Parts of Nickel-cadium alkaline cell.
1–active material 2–ebonite spacer sticks 3–pocket element 4–positive plates 5–positive terminal post 6–vent plug 7–negative terminal post 8–cover 9–container 10–negative plates 11–ebonite plate.

are well-suited for pleasure yatches and launches which may be laid up for long periods. They are also used in commercial airliners, military aeroplanes and helicopters for starting main engines or auxiliary turbines and for emergency power supply.
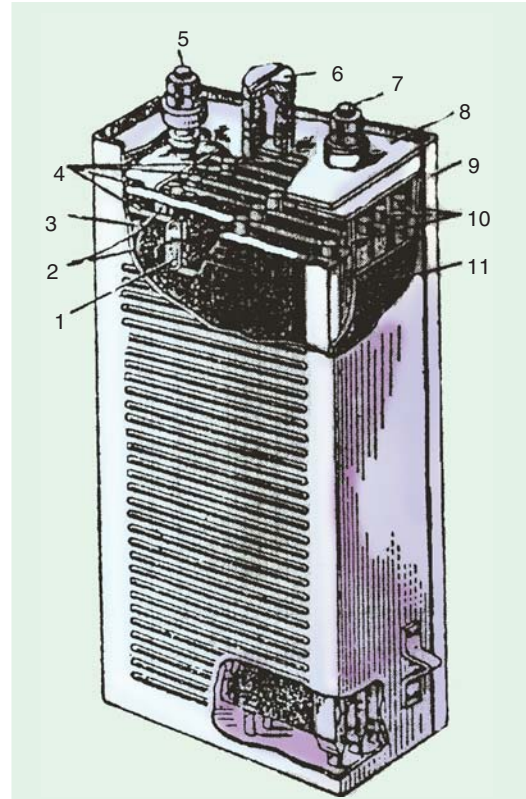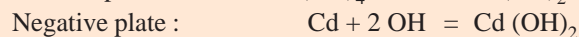
9.42. Chemical Changes

The chemical changes are more or less similar to those taking place in nickel-iron cell. As before, the electrolyte is split up into positive K ions and negative OH ions. The chemical reactions at the two plates are as under :

During discharge

Positive plate :	$Ni(OH)_4 + 2K = Ni(OH)_2 + 2 KOH$
Negative plate :	$Cd + 2 OH = Cd (OH)_2$

During Charging

Positive plate :	$Ni(OH)_2 + 2OH = Ni(OH)_4$
Negative plate :	$Cd(OH)_2 + 2 K = Cd + 2 KOH$
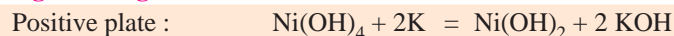
The above reaction can be represented by the following reversible equation :

$$Ni(OH)_4 + KOH + Cd \rightleftharpoons Ni(OH)_2 + KOH + Cd(OH)_2$$
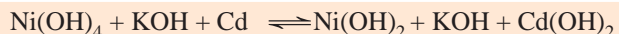
9.43. Comparison : Lead-acid and Edison Cells

The relative strong and weak points of the cells have been summarised below :

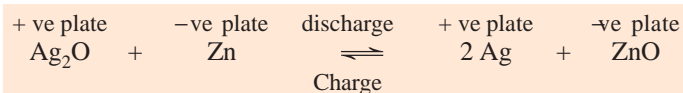| *Particulars*	*Lead-acid cell*	*Edison cell*
1. Positive Plate	PbO_2 lead peroxide	Nickel hydroxide $Ni(OH)_4$ or NiO_2
2. Negative Plate	Sponge lead	Iron
3. Electrolyte	diluted H_2SO_4	KOH
4. Average e.m.f.	2.0 V/cell	1.2 V/cell
5. Internal resistance	Comparatively low	Comparatively higher
6. Efficiency :	90–95%	nearly 80%
amp-hour watt-hour	72–80%	about 60%
7. Cost	Comparatively less than alkaline line cell	almost twice that of Pb-acid cell Easy maintenance
8. Life	gives nearly 1250 charges and discharges	five years at least
9. Strength	Needs much care and maintenance. Sulphation occurs often due to incomplete charge of discharge.	robust, mechanically strong, can withstand vibration, is light, unlimited rates of charge and discharge. Can be left discharged, free from corrosive liquids and fumes.

Moreover, as copmpared to lead-acid, the alkaline cells operate much better at low temperature, do not emit obnoxious fumes, have very small self-discharge and their plates do not buckle or smell.

9.44. Silver-Zinc Batteries

The active material of the positive plates is silver oxide which is pressed into the plate and then subjected to a heat treatment. The active material of the negative plates is a mixture of zinc powder and zinc oxide.

The chemical changes taking place within the cell can be represented by the following single equation :

$$\underset{Ag_2O}{\overset{+\,ve\ plate}{}} + \underset{Zn}{\overset{-ve\ plate}{}} \underset{Charge}{\overset{discharge}{\rightleftharpoons}} \underset{2\ Ag}{\overset{+\,ve\ plate}{}} + \underset{ZnO}{\overset{-ve\ plate}{}}$$

A silver-zinc cell has a specific capacity (*i.e.* capacity per unit weight) 4 to 5 times greater than that of other type of cells. Their ground applications are mainly military *i.e.* communications equipment, portable radar sets and night-vision equipment. Moreover, comparatively speaking, their efficiency is high and self-discharge is small. Silver-zinc batteries can withstand much heavier discharge currents than are permissible for other types and can operate over a temperature range of $-20°$ C to $+ 60°$C. Hence, they are used in heavy – weight torpedoes and for submarine propulsion. It has energy density of 150 Wh/kg. Its life time in wet condition is 1-2 years and the dry storage life is upto 5 years. However, the only disadvantage of silver-zinc battery or cell is its higher cost.

9.45. High Temperature Batteries

It is a new group of source which requires operating temperatures above the embient. They possess the advantages of high specific energy and power coupled with low cost. They are particularly suitable for vehicle traction and load levelling purpose in the electric supply industry. We will beiefly describe the following cell from which high-temperature batteries are made.

1. *Lithium/Chlorine Cell*

It has an emf of 3.5 V, a theoretical specific energy of 2200 Wh/kg at 614°C and operating temperature of 650°C.

2. *Lithium/Sulphur Cell*

It has an emf of 2.25 V, specific energy of 2625 Wh/kg and an operating temperature of 365°C.

3. *Lithium-Aluminium/Iron-Sulphide Cells*

The emf of these cells is 1.3 V and a theoretical specific energy of 450 Wh/kg.

4. *Sodium/Sulphur Cells*

It utilises liquid sodium as negative electrode and sulphur as positive electrode and employs polycrystalline beta alumina as solid electrolyte. It was conceived in the 1960s by J.T. Kummer and N. Weber. The cell reaction can be written as $2 Na + 3 S = Na_2S_3$. The announcement of sodium/sulphur battery based on beta alumina was made by Ford Motor Company of USA in 1966. The open-circuit voltage of the cell is 2.1 V and it has a specific energy of 750 Wh/kg with an operating temperature of 350°C. The two unique features of this cell are (1) a Faradaic efficiency of 100% and an ampere-hour capacity which is invariant with discharge rate and (2) high self-life (which is critical for certain space applications).

9.46. Secondary Hybrid Cells

A hybrid cell may be defined as a galvanic electrotechnical generator in which one of the active reagents is in the gaseous state *i.e.* the oxygen of the air. Such cells take advantage of both battery and fuel cell technology. Examples of such cells are :

1. *Metal-air cells such as iron oxygen and zinc oxygen cells.*

The Zn/O_2 cell has an open-circuit voltage of 1.65 V and a theoretical energy density of 1090 Wh/kg. The Fe/O_2 cell has an OCV of 1.27 V and energy density of 970 Wh/kg.

2. *Metal-halogen cells such as zinc-chlorine and zinc-bromine cells.*

The zinc-chlorine cell has an OCV of 2.12 V at 25°C and a theoretical energy density of 100 Wh/kg. Such batteries are being developed for EV and load levelling applications. The zinc-bromine cell has an OCV of 1.83 V at 25°C and energy density of 400 Wh/kg.

3. *Metal-hydrogen cells such as nickel-hydrogen cell.*

Such cells have an OCV of 1.4 V and a specific energy of about 65 Wh/kg. Nickel-hydrogen batteries have captured large share of the space battery market in recent years and are rapidly replacing Nickel/cadmium batteries as the energy storage system of choice. They are acceptable for geosynchronous orbit applications where not many cycles are required over the life of the system (1000 cycles, 10 years).

The impetus for research and development of metal-air cells has arisen from possible EV applications where energy density is a critical parameter. An interesting application suggested for a secondary zinc-oxygen battery is for energy storage on-board space craft where the cell could be installed inside one of the oxygen tanks thereby eliminating need for gas supply pipes and valves etc. These cells could be recharged using solar converters.

Some of the likely future developments for nickel-hydrogen batteries are **(1)** increase in cycle life for low earth orbit applications upto 40,000 cycles (7 years) **(2)** increase in the specific energy upto 100 W/kg for geosynchronous orbit applications and **(3)** development of a bipolar nickel-hydrogen battery for high pulse power applications.

9.47. Fuel Cells

As discussed earlier, a secondary battery produces electric current by oxidation-reduction chemical reaction. Similar chemical reactions take place in fuel cells but there is a basic difference between the two. Whereas in secondary batteries the
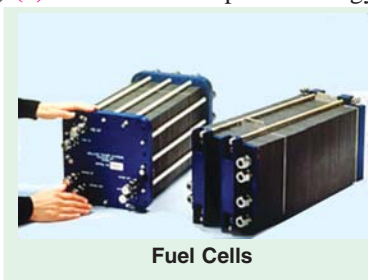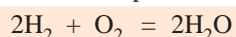

Fuel Cells

chemical energy is stored in the positive and negative electrodes, in fuel cells the oxidant and the fuel are stored outside the cells and must be fed to the electrodes continuously during the time the fuel cell supplies electric current. This gives an advantage to the fuel cells over the storage battery because fuels can be quickly replenished which is similar to filling up to the petrol tank of a car. Moreover, storage batteries when fully discharged take several hours to be recharged.

9.48. Hydrogen-Oxygen Fuel Cells

The first fuel battery was designed by F.T. Bacon in 1959. The construction of a simple fuel cell is shown in Fig. 9.32. The electrodes are made from sintered nickel plates having a coarse pore surface and a fine pore surface, the two surfaces being for gas and electrolyte respectively. The electrolyte used in KOH is of about 85 per cent concentration. The water vapour formed as a byproduct of the reaction is removed by condensation from the stream of hydrogen passing over the back of the fuel.

Fig. 9.32

The two electrodes of the fuel cell are fed with a continuous stream of hydrogen and oxygen (or air) as shown. The oxygen and hydrogen ions react with the potassium hydroxide electrolyte at the surface of the electrodes and produce water. The overall cell reaction is

$$2H_2 + O_2 = 2H_2O$$

The basic reaction taking place in the cells are shown in more details in the Fig. 9.32.

Fuel cell batteries have been used in the manned Apollo space mission for on-board power supply and also for power supply in unmanned satellites and space probes. These batteries have also been used for tractors, fork-lift trucks and golf carts etc. Research is being carried out to run these batteries with natural gas and alcohol. Fuel cell systems are particularly useful where electrical energy is required for long periods. Such applications include **(1)** road and rail traction **(2)** industrial trucks **(3)** naval craft and submarine **(4)** navigational aids and radio repeater stations etc.

9.49. Batteries for Aircraft

The on-board power requirements in aircraft have undergone many changes during the last three or four decades. The jet engines of the aircraft which require starting currents of about 1000 A, impose a heavy burden on the batteries. However, these days this load is provided by small turbogenerator sets and since batteries are needed only to start them, the power required is much less. These batteries possess good high-rate capabilities in order to supply emergency power for upto 1 h in the event of the generator failure. However, their main service is as a standby power for miscellaneous on-board equipment. Usually, batteries having 12 cells (of a nominal voltage of 24 V) with capacities of 18 and 34 Ah at the 10 h rate are used. In order to reduce weight, only light-weight high-impact polystyrene containers and covers are used and the cells are fitted with non-spill ventplugs to ensure complete unspillability in any aircraft position during aerobatics. Similarly, special plastic manifolds are moulded into the covers to provide outlet for gases evolved during cycling.

9.50. Batteries for Submarines

These batteries are the largest units in the traction service. In older types of submarines, the lead storage battery was the sole means of propulsion when the submarine was fully submerged and, additionally supplied the 'hotel load' power for lights, instruments and other electric equipment. When the introduction of the snorkel breathing tube made it possible to use diesel engines for propulsion, battery was kept in reserve for emergency use only. Even modern nuclear-powered submarines use storage batteries for this purpose. These lead-acid batteries may be flat, pasted plate or tubular
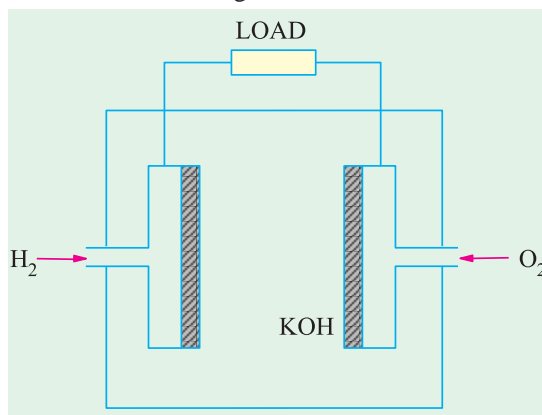
positive plate type with 5 h capacities ranging from 10,000 to 12,000 Ah. One critical requirement for this service is that the rate of evolution of hydrogen gas on open-circuit should not exceed the specified low limit.

Double plate separation with the help of felted glass fibre mats and microscoporous separators is used in order to ensure durability, high performance and low standing losses.

OBJECTIVE TESTS – 9

1. Active materials of a lead-acid cell are :
   - (a) lead peroxide
   - (b) sponge lead
   - (c) dilute sulphuric acid
   - (d) all the above

2. During the charging of a lead-acid cell :
   - (a) its cathode becomes dark chocolate brown in colour
   - (b) its voltage increases
   - (c) it gives out energy
   - (d) specific gravity of H_2SO_4 is decreased

3. The ratio of Ah efficiency to Wh efficiency of a lead-acid cell is :
   - (a) always less than one
   - (b) just one
   - (c) always greater than one
   - (d) either (a) or (b)

4. The capacity of a cell is measured in :
   - (a) watt-hours
   - (b) watts
   - (c) amperes
   - (d) ampere-hours

5. The capacity of a lead-acid cell does NOT depend on its :
   - (a) rate of charge
   - (b) rate of discharge
   - (c) temperature
   - (d) quantity of active material

6. As compared to constant-current system, the constant-voltage system of charging a lead-acid cell has the advantage of :
   - (a) avoiding excessive gassing
   - (b) reducing time of charging
   - (c) increasing cell capacity
   - (d) both (b) and (c).

7. Sulphation in a lead-acid battery occurs due to:
   - (a) trickle charging
   - (b) incomplete charging
   - (c) heavy discharging
   - (d) fast charging

8. The active materials of a nickel-iron battery are.
   - (a) nickel hydroxide
   - (b) powdered iron and its oxides
   - (c) 21% solution of caustic potash
   - (d) all of the above.

9. During the charging and discharging of a nickel iron cell :
   - (a) its e.m.f. remains constant
   - (b) water is neither formed nor absorbed
   - (c) corrosive fumes are produced
   - (d) nickel hydroxide remains unsplit

10. As compared to a lead-acid cell, the efficiency of a nickel-iron cell is less due to its :
    - (a) lower e.m.f.
    - (b) smaller quantity of electrolyte used
    - (c) higher internal resistance
    - (d) compactness.

11. Trickle charging of a storage battery helps to :
    - (a) prevent sulphation
    - (b) keep it fresh and fully charged
    - (c) maintain proper electrolyte level
    - (d) increase its reserve capacity

12. A dead storage battery can be revived by :
    - (a) a dose of H_2SO_4
    - (b) adding so-called battery restorer
    - (c) adding distilled water
    - (d) none of the above

13. The sediment which accumulates at the bottom of a lead-acid battery consists largely of :
    - (a) lead-peroxide
    - (b) lead-sulphate
    - (c) antimony-lead alloy
    - (d) graphite

14. The reduction of battery capacity at high rates of discharge is primarily due to :
    - (a) increase in its internal resistance
    - (b) decrease in its terminal voltage
    - (c) rapid formation of $PbSO_4$ on the plates
    - (d) non-diffusion of acid to the inside active materials.

15. Floating battery systems are widely used for :
    - (a) power stations
    - (b) emergency lighting
    - (c) telephone exchange installation
    - (d) all of the above

16. Any charge given to the battery when taken off the vehicle is called :
    - (a) bench charge
    - (b) step charge
    - (c) float charge
    - (d) trickle charge

ANSWERS

1. d **2.** b **3.** c **4.** d **5.** a **6.** d **7.** b **8.** d **9.** b **10.** c **11.** b **12.** d **13.** c **14.** c **15.** d **16.** a

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