29

Batteries

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29.1 Introduction

Electrochemical science is an interdisciplinary subject, which is unique both in its concepts (the chemical interactions between matter and electrons particularly across interfaces) and general in its applications. Electrochemical reactors use electrical energy to isolate elements from their compounds, as in the electro winning of metals (copper, silver, aluminium) or chlorine, or the production of hydrogen and/or oxygen by the electrolysis of water. On the other hand electrochemical power sources, batteries and fuel cells store chemical energy, which can be instantly converted into d.c. electrical energy. Corrosion, an electrochemical process, wastes both energy and materials.

29.2 Cells and batteries

29.2.1 Definitions

The term 'battery' means an assembly of voltaic primary or secondary cells. Batteries of secondary cells are known also as storage batteries or accumulators.

- A primary cell is used once until it is discharged and then discarded.
- A secondary cell needs to be charged after it is made before use. Once discharged the cell can be recharged and used again.

29.2.1.1 Terminology

Open-circuit voltage is the voltage at the terminal of the cell when no current flows, i.e. without an external loading circuit connected. It depends on the operating history of the cell, but cells are usually designed to have a relatively flat discharge curve until the cell is almost totally discharged after which the voltage drops quickly.

Cell capacity is the amount of energy, usually stated in ampere-hours that the cell can provide without the terminal voltage falling below a specified value. This is also stated as its 'C' rate which is the rate at which a fully charged cell would be discharged in one hour, i.e. a 5 Ah cell would have a C rating of 5 A.

Depth of discharge is the percentage of the cell's capacity which has been discharged.

Shelf life is a measure of the ability of the cell to retain its charge under the storage conditions encountered.

Cycle life is the number of charge/discharge cycles a secondary cell can tolerate before performance failure.

Charge acceptance is the proportion of the charge input which the cell can give out again without the voltage falling below a specified value, i.e. is a measure of the ability of a cell to accept charge.

Charge voltage is the voltage developed across a secondary cell when it is under charge. This voltage can be up to 50% higher than the rated discharge voltage of the cell. It increases with the charge rate and with low temperatures.
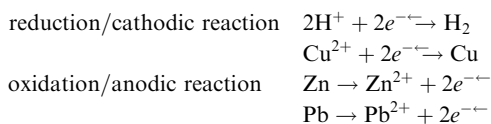
29.2.2 Principles

In both primary and secondary batteries the individual cells consist of a positive and negative electrode immersed in an ion-conducting medium called the electrolyte and generally separated by a porous non-conducting diaphragm, called the separator. The electrodes, which must be electrically conducting, may consist of a single rod or plate, or a number of these welded or bolted together in parallel. In some cells (for example, the conventional primary 'dry' cell) the outer metal container may constitute one of the electrodes. The two electrodes have different electrical potentials when immersed in the common electrolyte and the difference between these potentials represents the e.m.f., or open-circuit voltage, of the cell.

In both primary and secondary cells the electrical energy released during discharge is derived from the chemical energy liberated as a result of the chemical reactions taking place in the cell. These reactions involve charged particles in the electrolyte, known as 'ions'. Ions, if positively charged, have a deficiency of electrons, and if negatively charged, carry an excess of electrons. As indicated below, certain ions tend to react with the electrode in their vicinity, causing a transfer of electrons from ions to electrode, or vice versa. If this reaction is allowed to proceed (for example, by closing the external circuit to which the battery is connected), the transfer of electrons from one electrode to the other gives rise to an electric current flowing in the external circuit conventionally from the positive to the negative electrode: the flow of electrons is in the opposite direction. Thus, an *anodic* reaction involving the release of electrons occurs at the *negative* electrode, and a *cathodic* reaction involving the capture of electrons at the *positive* terminal of the battery. In electrochemical reactors the reverse is true, i.e. *anodic* reaction at the *positive* and *cathodic* at the *negative* electrode.

29.2.3 Redox process

The chemical reactions at the electrodes are either 'reduction' or 'oxidation', i.e. 'redox' processes. The basic feature of such reactions is the gain or loss, respectively, of one or more electrons, e.g.

reduction/cathodic reaction $\quad 2H^+ + 2e^- \rightleftharpoons H_2$
$$Cu^{2+} + 2e^- \rightleftharpoons Cu$$
oxidation/anodic reaction $\quad Zn \rightarrow Zn^{2+} + 2e^-$
$$Pb \rightarrow Pb^{2+} + 2e^-$$

Here e represents the electron. H, Cu, Zn and Pb represent atoms, or (when charged) ions of hydrogen, copper, zinc and lead. The sign $+$ indicates a deficiency of one electron; $2+$ indicates a deficiency of two electrons.

The gaseous hydrogen formed by the first reduction process, if allowed to accumulate, would rapidly polarise the electrode, and the electrochemical reaction would virtually cease. To overcome this, the positive electrodes of many kinds of batteries are selected from substances which readily undergo a depolarising reaction with hydrogen. Typical examples are manganese dioxide (MnO_2), used in the primary dry battery, and lead dioxide (PbO_2), used in the lead/acid storage battery. Negative electrodes must be readily oxidisable, and for these active metals such as zinc, lead and cadmium are generally chosen.

Electrode potentials and redox reactions are not confined to metals, but include such elements as hydrogen, oxygen, chlorine or fluorine, either in the gaseous form or in combination with some metal in the form of an inorganic salt.
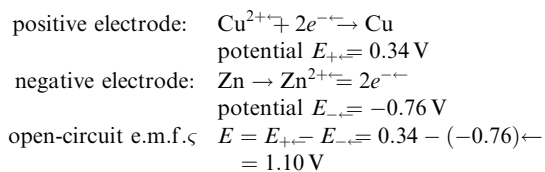
Electrode potentials are generally expressed with respect to hydrogen, which for standard conditions is assigned a potential of zero. It is an advantage to have at the two electrodes redox reactions widely spaced on the potential scale to give the highest cell e.m.f. But the choice is restricted by other factors—in particular, the type of electrolyte. Formerly electrolytes were aqueous solutions of salts, acids or bases. Organic electrolytes (e.g. propylene carbonate containing ionic conductors) and molten salts (e.g. LiCl–KCl eutectic, which melts at 352°C) are now being used, so that more active 'anodes' such as lithium or its alloys, which react with aqueous solutions, can be incorporated.

29.3   Primary cells

Primary cells differ from secondary cells in that the electrochemical reactions are not reversible, or, if so, only to a very limited extent. This may be primarily due to physical factors such as a loss of electrical contact by the chemical products of the discharge. In the case of the primary conventional 'dry' cell, for example, failure often occurs through excessive corrosion of the zinc can which forms one of the electrodes. In secondary cells or accumulators the reactions are readily reversible. The original chemical compounds can be re-formed by passing a direct current through the cell in the reverse direction, and accumulators can generally be submitted to many cycles of discharge and charge in this way.

The simplest primary cell, and one of the earliest (1836), is the *Daniell* cell, named after its inventor. Since many of the principles involved are common to other systems, this cell will be described in some detail. The electrodes are copper and zinc, and the electrolyte is a solution containing sulphate ions. The copper electrode is immersed in a solution of copper sulphate held in an inner porous pot, and the zinc electrode is held in a solution of zinc sulphate or dilute sulphuric acid in the outer glass vessel. The cell is shown diagrammatically in *Figure 29.1*.

The chemical reactions on discharge can be represented as follows:

positive electrode: $Cu^{2+} + 2e^- \rightarrow Cu$
potential $E_+ = 0.34\,V$

negative electrode: $Zn \rightarrow Zn^{2+} + 2e^-$
potential $E_- = -0.76\,V$

open-circuit e.m.f. $E = E_+ - E_- = 0.34 - (-0.76)$
$= 1.10\,V$

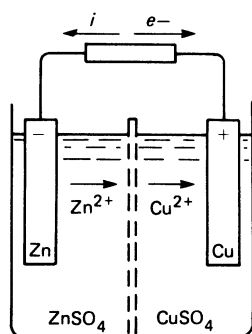Early forms of this cell were made with both electrodes immersed in dilute sulphuric acid, and had somewhat different reactions: the main reaction at the negative electrode was (as above) the formation of positively charged Zn ions, but in the presence of the acid (H_2SO_4) hydrogen was also produced, by a corrosion reaction. At the positive electrode the reaction was $2H^+ + 2e^- \rightarrow H_2$: and as the discharge reaction proceeded, hydrogen gas accumulated on the electrode surface, polarising the cell and depressing the terminal voltage. Other factors in the voltage 'fall-off' are (a) overvoltages arising from the kinetic limitations of the electrode reactions themselves, (b) the slow diffusive mass transfer of the ions up to the electrode surfaces, and (c) the ohmic resistance of the electrolyte. Substituting sulphuric acid by copper sulphate ensured that copper and not hydrogen ions were discharged at the positive electrode, eliminating the counter-e.m.f. By placing the zinc electrode in its own zinc sulphate electrolyte, the evolution of hydrogen was eliminated; but this made it necessary to enclose the copper electrode and its electrolyte in a porous pot, increasing the ohmic resistance of the cell.

### 29.3.1   Leclanché (zinc–carbon) cell

In its 'dry' form, the Leclanché cell is the most common. A zinc plate or container forms the negative, a carbon plate or rod the positive electrode. The electrolyte is aqueous ammonium chloride. Through ionisation of the water, hydrogen and hydroxyl ions are produced ($H_2O \rightarrow H^+ + (OH)^-$). During the discharge the zinc electrode is oxidised in the reaction

$Zn + 2(OH)^- \rightarrow Zn(OH)_2 + 2e^-$
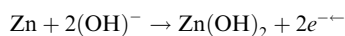
and hydrogen migrates to the carbon. Polarisation is avoided by surrounding the carbon by manganese dioxide, which participates in the redox reaction

$2MnO_2 = 2H^+ + 2e^- \rightarrow Mn_2O_3 + H_2O$
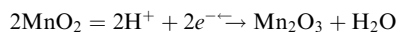
and the complete cell reaction, in which the electrolyte is also involved is

$2MnO_2 + 2NH_4Cl + Zn \rightarrow 2MnOOH + Zn(NH_3)_2Cl_2$
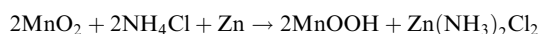
corresponding to an open-circuit e.m.f. of about 1.5 V. The presence of zinc and ammonium chlorides in the electrolyte keeps the acidity at the right level and helps to reduce polarisation of the zinc electrode by the flocculent jelly-like zinc hydroxide that would otherwise coat the surface. In practice, the cells are not strictly 'dry', as the electrolyte is a thick paste. The cell (*Figure 29.2*) comprises: (a) a central rod forming the positive terminal; (b) a depolariser of manganese dioxide (mixed with graphite or a highly active form of carbon black known as acetylene black to improve its
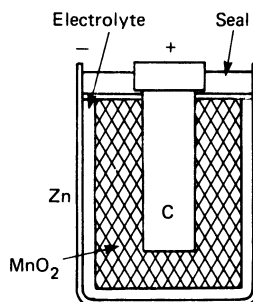

Figure 29.1   Daniell cell

Figure 29.2   'Dry' Leclanché cell

conductivity) that is liberally moistened by the electrolyte; (c) a thin layer of jellified electrolyte; (d) a hard-drawn zinc outer can forming the negative terminal; and (e) a seal, such as a card disc covered by a layer of bitumastic compound. Recent improvements, particularly in high rate performance, have been achieved by the replacement of the bulk of the ammonium chloride in the electrolyte with zinc chloride.

29.3.1.1 Performance

In many applications the use is intermittent. Polarisation develops as the current flows; during rest periods the cell recovers. *Figure 29.3* shows typical curves for a U2 cell discharging continuously through a lamp, the resistance of which varied from 1.32 to 1.03 Ω during the discharge. The cell dimensions are 32 mm diameter, 57 mm height and 0.1 kg mass. Cell behaviour in store and in transit ('shelf life') is lengthened by adding a soluble mercury salt to the electrolyte, which lightly amalgamates the active surface of the zinc container. Shelf life is reduced with high, and extended with low, ambient temperatures.

29.3.1.2 Flat and layer cells

Flat and layer cells have been developed for transistorised electronic equipments. In a duplex type the positive and the negative electrodes are placed on opposite sides of an electrically conducting diaphragm impermeable to the electrolyte. In the layer-built battery the zinc plate serves as the conducting diaphragm as well as the negative plate. On the opposite side this is first coated with a thin adherent layer of carbon mixed with a plastic resin, which functions much as the carbon rod in the cylindrical cell. Against this carbon layer is placed a moulded cake of the usual black depolariser mix and next to it a layer of absorbent material, such as filter paper, impregnated with the electrolyte. Another duplex electrode is placed on top of the first, and in this way a multicell battery of any desired voltage can be built up.

Sealing presents a particular difficulty with layer-built batteries. Obviously, there must be no electrical contact between the electrolytes of neighbouring cells, as this would permit leakage current. Also, some provision must be made for the release of adventitious gas from each cell. One means of sealing is to separate the adjoining duplex electrodes with annular spacing pieces and to cover the edges of the whole battery in wax or a suitable cold-setting plastic resin. Another way is to encapsulate the unit in a tightly stretched plastic stocking which is shrunk into position by gentle heat after application. Yet another method is
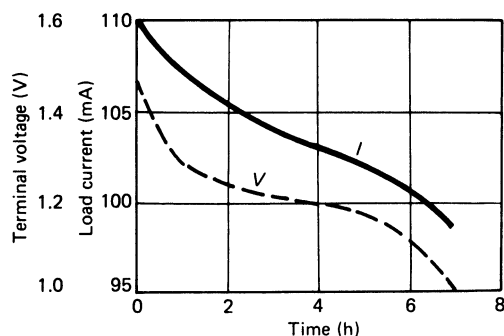
to enclose the edges of each duplex diaphragm in an annular envelope of rubber or a plastic material, shrunk into position by heat. To reduce the risk of leakage, such envelopes may be cemented to the diaphragm and the assembled unit sealed together or firmly wrapped with plastic tape. Thin strips of rubber or suitable plastic materials in this form are sufficiently permeable to hydrogen to allow the release of gas, and the construction allows for sufficient expansion to release any internal pressures that may develop, without permitting significant leakage of electrolyte.

29.3.2 Standard cells

The Weston standard cell (*Figure 29.4*) has a cadmium/cadmium sulphate negative electrode, an electrolyte of cadmium sulphate and a mercury/mercurous sulphate positive electrode. To give added stability, the cadmium is amalgamated with mercury and the cell assembled in an H-shaped glass vessel with platinum leads to the terminals. The cadmium and mercury sulphates are usually prepared as thick pastes by digesting fine crystals of the salts with cadmium sulphate solution. Small quantities of sulphuric acid are added to reduce any tendency of the salts to hydrolyse.
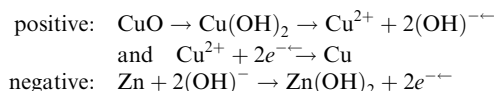
When a saturated solution is used for the electrolyte, the cell is termed 'normal' and has an e.m.f. of 1.01862 V at 20°C (for e.m.f.s at other temperatures see reference 2).

29.3.3 Alkaline cells

Three alkaline cells use zinc for the negative electrode.

29.3.3.1 Copper oxide/zinc

The positive electrode or depolariser is CuO, the electrolyte a solution of caustic soda of relative density about 1.2. The cell was formerly common in railway signalling, being cheap to make and able to deliver intermittent currents over considerable periods. The open-circuit e.m.f. is about 1.0 V, and on load 0.5–0.7 V. The reaction at the positive electrode involves the reduction of the copper oxide, while at the negative the zinc is oxidised:

positive: $CuO \rightarrow Cu(OH)_2 \rightarrow Cu^{2+} + 2(OH)^{-\leftarrow}$
and $Cu^{2+} + 2e^{-\leftarrow} \rightarrow Cu$
negative: $Zn + 2(OH)^- \rightarrow Zn(OH)_2 + 2e^{-\leftarrow}$

29.3.3.2 Silver oxide/zinc

The silver oxide/zinc cell has military and other special fields of application. With appropriate modifications this couple will also function as a reversible cell, at any rate for a limited number of cycles. Batteries of cells have outputs four to five times those of any other system for the same weight and
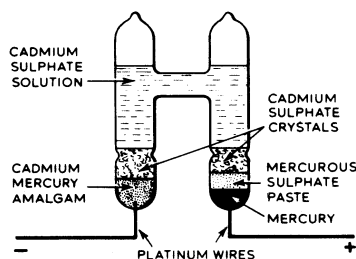

Figure 29.3 Discharge of a U2 cell

Figure 29.4 Weston standard cell

volume, and they are particularly in demand where very high currents and a low weight and volume are required, as in torpedo batteries, guided missiles and space satellites. In the primary form the batteries may be stored dry for long periods and brought into action by priming with electrolyte either by some pressure device or simply under the influence of gravity. To reduce polarisation, the electrodes are generally made porous. In one method of manufacture the positive electrode is made by sintering silver powder, the porous compact then being anodised to convert it to silver peroxide (Ag_2O_2). The zinc electrode is made from a paste of zinc oxide and caustic potash solution which is pressed into a screen of a suitable metal, such as silver or silver-plated copper. This is then reduced electrolytically to spongy zinc in dilute alkali solution. The electrolyte is caustic potash solution of about 30% concentration. A thin separator made of cellophane or paper may be used to prevent the plates from coming into contact and causing a short-circuit.

The discharge reactions at the electrodes are analogous to those already described for the copper oxide/zinc cell, but the silver peroxide passes through an intermediate stage to silver oxide (Ag_2O) before being reduced completely to metallic silver. The two separate reduction stages each have their own characteristic potential, so the discharge voltage curve of the cell with freshly prepared electrodes has two plateaux, a short one at about 1.80 V and a much longer one at about 1.50 V. The second portion of the discharge at about 1.50 V per cell or less, depending on the rate, remains remarkably steady until the active materials are exhausted, when the cell voltage falls sharply.

29.3.3.3 Mercury oxide/zinc

The electrolyte is caustic potash, but the elements are merely moistened. Known as the Ruben–Mallory cell, the mercury oxide/zinc cell has very low standing loss and gives steady voltages for long periods on low discharge rates. For such applications as hearing aids it is made in the form of a small metal button; as batteries of 6–8 V the applications are to portable transistorised radio receivers and 'walkie-talkie' sets. Mercuric oxide (HgO), mixed with 5–10% graphite to increase conductivity, acts as the positive depolariser. The mixture is compressed into a pellet, and in the button form this is placed in contact with the steel cup that makes one half of the button. A pellet of compressed zinc powder with a small amount of mercury is in contact with the other metal half of the button, which may be of copper. The separator may be a layer of absorbent paper saturated with the caustic potash solution. The outer surfaces of the two metals are insulated from each other by a plastic grommet, and form the terminals. Such sealed buttons have a capacity of a few milliampere-hours. In other forms the zinc electrode may be a coiled strip or perforated sheet, and the electrolyte is a jelly with gelling agents such as carboxymethylcellulose. The reactions are similar to those of other alkaline couples:

positive: $HgO + H_2O + 2e^- \rightarrow Hg + 2(OH)^-$

negative: $Zn + 2(OH)^- \rightarrow Zn(OH)_2 + 2e^-$
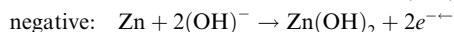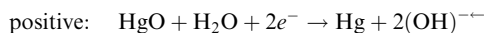
The open-circuit cell e.m.f. is 1.35 V, and the terminal voltage on load is 1.25–1.0 V. Prolonged low-rate discharges are obtainable. Standing losses are very low.

29.3.3.4 Air depolarised

These systems are essentially hybrids between true batteries which contain both electrode materials within themselves and fuel cells (see Section 29.5) which contain neither. In principle, they exhibit very high energy densities. In practice, however, various problems have been encountered, such as polarisation of the air cathode.

Zinc–air batteries (see below) have been the most successful, but aluminium–air, iron–air and lithium–air systems all have their protagonists. Lithium must be employed in strongly alkaline solutions to avoid reactions with the aqueous cell electrolyte. Aluminium–air systems are particularly attractive, at least in principle. In this case it is envisaged that the aluminate solutions which are produced as the batteries are discharged would be recycled to the aluminium smelters and 'fuel' (e.g. aluminium foil) would, if the batteries were used for traction, be obtained at suitable aluminium filling stations(!) during a journey to replace that used in the cells. The aluminate solutions could be tapped off at the same time.

Analogous to the carbon/zinc Leclanché cell, the air depolarised cell uses atmospheric oxygen as depolariser for the porous carbon electrode, which is made by roasting finely divided carbon and charcoal with a binder and then wet-proofing (e.g. by paraffin wax) to render the interior hydrophobic. The carbon electrode is only partially immersed in the electrolyte, and oxygen is readily adsorbed from the air. The negative electrode, of large plates of zinc lightly amalgamated with mercury, is completely immersed. A cell generally consists of two zinc plates flanking one carbon electrode, with capacities up to several hundred ampere-hours.

One range of cells has as electrolyte a solution of caustic soda. The essential reaction at the positive (oxygen) electrode is the reduction of oxygen with the production of $(OH)^-$ ions, and at the negative (zinc) electrode these contribute to the usual oxidation reaction, as in the copper oxide/zinc cell. The open-circuit e.m.f. is about 1.45 V; the terminal voltage on load for small currents is about 1.3 V, reducing to about 1.1 V at the end of the discharge.

The Le Carbone AD cell has as electrolyte a solution of ammonium chloride, which reduces polarisation at the zinc electrode by the action of zinc hydroxide. Large batteries of this type have been used in European railway signalling.

29.3.3.5 Alkaline manganese batteries

Another important recent development, providing up to 50% more power than Leclanché cells of the same volume uses dilute KOH electrolyte in a manganese dioxide/zinc cell with a reverse type of electrode assembly. The zinc anode paste is held in a porous tubular separator surrounding the centrally placed current-collecting nail anode. The cathode mixture of MnO_2 and graphite is highly compressed in the form of annular tablets and these are packed concentrically around the zinc anode. The whole assembly is contained in a thin-walled steel can, with the usual plastic disc-bitumen closure. The extra capacity over standard cells is due to the greater amount of MnO_2 (40–70%) the absence of solid NH_4Cl and the higher conductivity of the KOH electrolyte.

29.3.4 Water activated cells

Water activated cells are stored dry for long periods, then activated by filling with (or immersion in) salt or fresh water; in the latter case, sodium or potassium chloride is included in the cell to increase its conductivity.

29.3.4.1 Silver chloride/magnesium

Silver chloride/magnesium cells are costly, but can deliver very large currents for short periods, typically for electric

torpedoes. When flooded with sea water, they become immediately active. The positive electrode (silver chloride) is a thin plate obtained by rolling a slab cast from the molten salt or by chloridising thin sheets of silver. The negative electrode is formed from magnesium strip or sheet. The electrodes are separated by rubber bands, absorbent paper, ebonite forks, or glass beads cemented to the electrode surface. Cylindrical cells with coiled plates have been used in batteries for meterological pilot balloons. During discharge, silver chloride is reduced to metallic silver and the chloride ions Cl^- migrate through the aqueous electrolyte to the negative (magnesium) electrode, which is oxidised to magnesium chloride ($MgCl_2 \cdot 6H_2O$), with the transfer of electric charge. The formation of silver raises the conductivity during discharge: this counteracts polarisation and tends to stabilise the terminal voltage. The e.m.f. is about 1.7 V, and the terminal voltage during discharge falls from 1.5 V to 1.0 V.

29.3.4.2 Copper chloride/magnesium

The chemical reactions are similar to those in the foregoing; the cell is cheaper, but the voltage is lower. Batteries of this type have been used in radar-sonde and other meteorological equipment. For higher voltage at low discharge currents a bipolar construction with duplex electrodes has been used. Positive plates are made by pressing the pelleted salt into copper screens or by dipping into molten chloride. Duplex electrodes are made by pressing or welding positive and negative electrodes to opposite sides of a thin copper foil.

29.3.4.3 Lead oxide/magnesium

The lead oxide/magnesium cell is simple, and comprises a fully formed lead dioxide positive plate (as in a lead/acid secondary cell) flanked by a U-shaped magnesium negative plate, with absorbent paper separators. The paper is impregnated with potassium chloride solution, then dried before assembly. The base of the element is left open and the cell is activated by dipping into fresh water for about 30 s. The electrode reactions are the reduction of lead dioxide to lead dioxide at the positive, and oxidation of magnesium to magnesium hydroxide at the negative, electrode. A two-cell battery for a pilot balloon lamp gives typically 0.3 A at 3.0 V for 30 min at temperatures down to 0°C. As the discharge reactions are exothermic, batteries can still operate in ambient temperatures of −40°C.

29.3.5 Acid cells

Primary cells with acid electrolytes have been developed for special military and meteorological requirements.

29.3.5.1 Lead oxide/zinc (or cadmium)/sulphuric acid

These cells can be stored 'dry' for long periods and activated as required, an advantage in radio-sonde equipment, meteorological balloons, telemetering in experimental guided missiles and similar special applications. Batteries are referred to as 'short-duration reserve'. Lead dioxide electrodes (like those in lead/acid secondary cells) are welded in parallel according to the capacity required, interleaved with sheets of zinc or cadmium, and separated by thick strips of absorbent paper. The sulphuric acid electrolyte, of relative density 1.270 at 15.5°C, can be introduced some hours before use. The chemical reactions involve the reduction of lead dioxide to lead sulphate and oxidation of the negative electrode to zinc (or cadmium) sulphate. The

cell e.m.f. is 2.5 V (with zinc) or 2.2 V (with cadmium). Corrosion of the zinc is reduced by amalgamation obtained by adding about 1% of mercuric sulphate to the electrolyte. The zinc couple gives higher voltage and discharge rate but at temperatures below 10°C, the zinc is polarised by the build up of a reaction product; and at higher temperatures local action is acute, standing loss is high and accelerated activity on discharge can lead to gas polarisation. The cadmium negative is less temperature sensitive, does not require amalgamation and gives satisfactory performance over the range 0–60°C. Typical voltages for a three-cell battery at 3 A discharge for 3 min are 6.8–6.5 V (zinc) and 6.3–6.0 V (cadmium).

29.3.5.2 Lead dioxide/lead/perchloric acid

Excellent discharge reactions are obtainable with perchloric (or fluoboric or fluosilicic) acid producing soluble lead compounds. Polarisation by the build up of reaction products is considerably reduced, so that it is not necessary to increase the surface of the electrodes by making them porous, as in a *secondary* cell. Nearly all of the active electrode material is usable, giving a high output/mass ratio. But for the same reason the cells must be used soon after priming, to avoid high standing loss. The cells are useful where they can be stored dry and primed immediately before use, and where low-mass batteries are required for large currents for relatively short periods. The positive plate is made by electrodepositing a thin non-porous film of lead dioxide on a sheet of nickel, iron or copper from a bath of lead perchlorate, lead nitrate or sodium plumbate. The negative plate may be made by electrodepositing thin layers of lead on a similar metal conductor, or directly from lead sheet. The plates are connected in parallel packs, the interleaved negatives being separated from the positives by spacers allowing rapid ingress of the electrolyte. The latter is held in compartments above the cell and allowed to enter the cell when the cell is primed. During discharge, lead dioxide is reduced to lead monoxide which is at once converted to lead perchlorate; the lead negative is oxidised to the same final product. Batteries have been constructed on the bipolar principle, the lead and lead dioxide being deposited on opposite sides of a nickel sheet. The e.m.f.s with electrolytes of 40–60% concentration range from 2.1 V (perchloric acid) to 1.9 V (fluoboric and fluosilicio acids). Perchloric acid in high concentration can become explosive in the presence of organic materials such as paper, sawdust, etc. Cells with the alternative electrolytes present no such risk, but have lower outputs.

29.4 Secondary cells and batteries

A secondary (or storage or accumulator) cell consists essentially of two electrodes held apart by separators and immersed in an electrolyte, the assembly being fitted into a suitable container. In the lead/acid cell the positive electrode is lead dioxide and the negative is pure lead in spongy form. In the alkaline cell the positive is nickel hydroxide and the negative is iron or cadmium. The electrolyte for the former cell is dilute sulphuric acid and for the latter, dilute potassium hydroxide.

29.4.1 Lead/acid cells

The chemical reactions follow the redox pattern (see Section 29.2.3). The current in the external circuit flows conventionally

from the positive to the negative electrode. The two reactions can be written as follows:

positive: $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

negative: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^{-\leftarrow}$
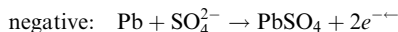
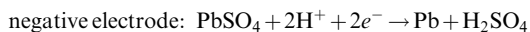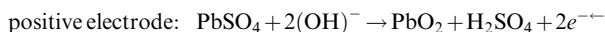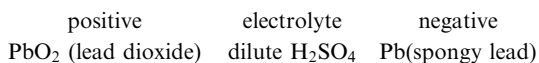The reversible potentials are $E_+ = +1.685\,V$ and $E_- = -0.356\,V$, giving an open-circuit e.m.f. $E = 2.041\,V$.

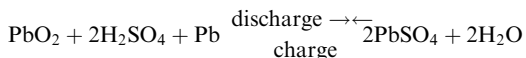### 29.4.1.1   Charge and discharge reactions

A secondary cell must be connected to a d.c. supply for charging, positive to positive and negative to negative. During *charging* the reactions are

positive electrode: $PbSO_4 + 2(OH)^- \rightarrow PbO_2 + H_2SO_4 + 2e^{-\leftarrow}$

negative electrode: $PbSO_4 + 2H^+ + 2e^- \rightarrow Pb + H_2SO_4$

The fully charged cell has

| positive | electrolyte | negative |
| PbO_2 (lead dioxide) | dilute H_2SO_4 | Pb(spongy lead) |

and the overall cell reactions are

$$PbO_2 + 2H_2SO_4 + Pb \;\overset{\text{discharge} \rightarrow}{\underset{\text{charge}}{\leftarrow}}\; 2PbSO_4 + 2H_2O$$

During *discharge* the active parts of both electrodes are converted to lead sulphate, and the concentration of the electrolyte is reduced by both the removal of sulphate ions and the formation of water. During *charge* the lead sulphate at the negative plate is reduced to spongy lead, and at the positive electrode to lead dioxide with the release of sulphate ions at both plates and an increase in the concentration of the electrolyte. Measurement of the concentration indicates the state of the electrodes: the relative density of the electrolyte is read by a hydrometer.

Typical charge/discharge cell voltages are shown in *Figure 29.5*. Lead sulphate, the product of the discharge reaction, is practically insoluble in the electrolyte, a factor that endows the cell with its high degree of reversibility. During cycling the lead sulphate remains where it is formed, and the structure of the active materials is relatively undisturbed.

29.4.1.2   Materials

Lead dioxide and spongy lead are the active materials, but it is necessary to provide metallic frames or supports for them. The success of the modern secondary cell depends on plate design and manufacture, and on the separators that prevent internal short-circuits and help to retain the active material in position.
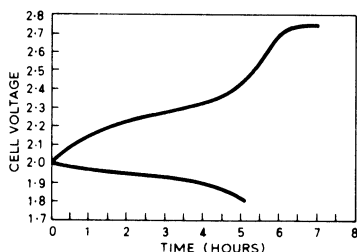

Figure 29.5   Typical charge and discharge voltages of a lead–acid cell

Plates

Planté (formed) plate   The positive plate has its effective surface area increased ten-fold by forming close-pitched fins on the surface of a pure lead plate. The negative plate was commonly of a 'box' form.

Faure (pasted) plate   The active material applied to open-mesh grids cast in antimonial lead is a paste made by mixing lead oxide with water and sulphuric acid. The plate is seasoned, dried and then electrochemically converted to lead dioxide or spongy lead by charging in dilute sulphuric acid. The grid acts both as a support for the active material and as the conductor of the current to and from the active material. The merit of the pasted plate is that the grid can be cast in precisely defined thin sections as low as 1.5 mm or less, and the ratio between active material and carrier grid is high. In addition to the standard gravity die-casting process, in modern developments, thin grids are made by stamping or punching suitable patterns from thin pure lead or lead-calcium alloy sheet. The red lead and litharge originally used for the positive and negative plates have been superseded by a grey oxide containing one-third fine metallic lead particles and two-thirds lead monoxide.

Reference has already been made to the box type of pasted negative plate used with Planté positive plates, in which the paste is held in the grid by thin sheets of perforated lead covering both surfaces. The box negative plate is however costly, both on materials and manufacture, and has now been largely superseded by the common pasted negative plate.

Separators   In some cells the separators serve only to keep the plates equidistant; in others they act as diaphragms to prevent internal short-circuit or to retain the active material.

Earlier wood separators have been almost entirely superseded by artificially made forms. One of the most successful is a microporous polyvinyl chloride (PVC). It has a high degree of diffusability, a low electrical resistance in acid and great durability under normal battery conditions. It is used in all types of lead/acid batteries. Another type of separator is made by sintering fine particles of PVC, and yet another by impregnating an absorbent paper with an acid-resistant resin such as phenol formaldehyde which both stiffens the paper and protects it against attack by the acid.

The profile of the separator is of interest. One product of the chemical reaction at the positive plate is water, the other being lead sulphate, which removes SO_4 ions from the electrolyte. The acid is doubly diluted at the positive plate, whereas at the negative only lead sulphate is formed. It is, consequently, necessary to provide a greater reservoir of acid adjacent to the positive plate, and in cells where the amount of acid is minimised it is usual to make separators with ribs which rest against the plate surface.

Electrolyte   Different concentrations of the sulphuric acid electrolyte may be used, depending on the application for which the particular battery has been designed. The voltage of the cell depends on the concentration of the electrolyte, being higher for higher concentrations. Also, the minimum electrical resistivity at 20°C occurs at a concentration of about 31%, equivalent to a density of 1.225; and the minimum freezing point at a relative density of 1.300. Taking these and other factors into account, stationary cells are generally filled with acid of relative density 1.200–1.215; automobile and traction batteries, 1.275–1.285, or in tropical climates 1.240–1.260.

One important operational aspect of the electrolyte concerns *impurities*. Impurities such as chloride and acetic or nitric acid attack the positive grids and are generally kept to a minimum in both the filling-in acid and the 'topping-up' water which is added to replace water lost by evaporation and by electrolysis during charging. Metals such as iron and manganese cause self-discharge of both positive and negative plates, while nickel and copper are 'plated out' on the negative and also cause self-discharge. Limits for various impurities are given in British Standards. For topping up, it is generally advisable to use only distilled water.

29.4.1.3 Construction

Battery design and construction is considerably influenced by the application.

Road vehicle starting, lighting and ignition A battery which is used for starting, lighting and ignition (SLI) must, *inter alia,* be able to deliver up to 100 A/h of electrical energy at the 20-h rate and be able to supply high currents (e.g. 400–450 A) for up to half a minute without too much voltage fall-off for engine start-up purposes. Faure plates have a special advantage where high currents are required. The larger the plate surface area, the lower the polarisation and the higher the cell voltage. Batteries normally comprise three-cell (6 V), six-cell (12 V) and 12-cell (24 V) assemblies, with plates connected in parallel groups in moulded containers.

In the past, batteries were supplied which, after filling with acid, required an extended first charge to reduce the active spongy lead negative plate. More recently, a dry-charged automobile battery has been developed to give about 75% of its nominal capacity shortly after filling, even after lengthy storage. The basic requirement in manufacture is to ensure a high percentage of lead dioxide in the positive plates and a minimum (e.g. 10%) of lead monoxide in the negative plates. This is achieved by the inclusion in the plates of an antioxidant, or by drying the plates after formation in an oven in which they cannot come into contact with atmospheric oxygen.

Traction These batteries often have larger voltages and higher capacities than the SLI type. Batteries for electric vehicles may have a flat-plate or an iron-clad tubular form. The application involves deeper cycling and causes shedding of the active material. In the Faure plate design, 'retainers' (generally of thickly matted glass-wool fibres) are placed in close contact with the surfaces of the positive plates. Batteries of this type (*Figure 29.6*) have lives of 6 years or more. With tubular plates (*Figure 29.7*) tubes of high porosity are fitted: one such plate uses non-woven fibres of a plastic inert to sulphuric acid, such as Terylene. Another type uses an inner woven stocking of glass fibre, strengthened by individual thin-walled perforated PVC tubes. By raising the permeability to acid, these designs have enabled the output/mass and output/volume ratios to be increased by 30% without loss of durability and cycling life.

29.4.2 Nickel/cadmium and nickel/iron alkaline cells

Both of these commercially available alkaline cells have the same electrolyte, dilute potassium hydroxide, and the same positive active material, nickel hydroxide. The nickel/cadmium cell has a negative plate of cadmium with a small proportion of iron. Both have an e.m.f. of about 1.2 V. Cadmium gives the nickel/cadmium cell a lower charging voltage and reduced ohmic resistance, and its characteristics
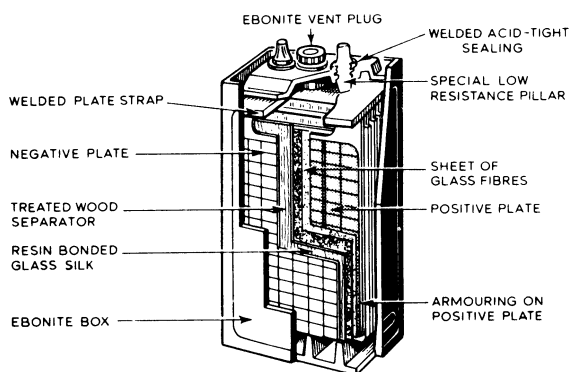
Figure 29.6 Sectional view of a traction cell
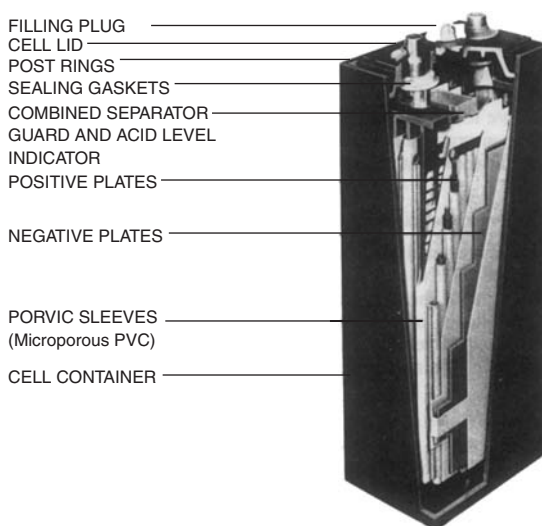
Figure 29.7 Iron clad cell with tubular positive plates

resemble those of the lead/acid cell. Use of the nickel/iron cell is mainly in traction, where the higher charging voltage and internal resistance are less important.

29.4.2.1 Charge and discharge reactions

The chemical reactions are complicated. The following gives a general guide:

positive: $2Ni(OH)_3 - H_2O \rightarrow 2NiOOH + 2H^+ + 2e^- \rightleftharpoons$
$2Ni(OH)_2$

negative: $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^- \leftarrow$
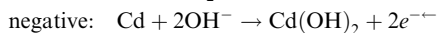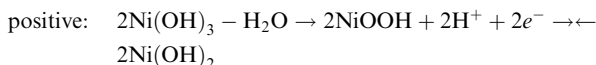
The reversible potentials of these reactions are respectively $E_+ = +0.49$ V and $E_- = -0.81$ V, giving an open-circuit e.m.f. per cell of $E = 1.30$ V. The overall reaction is

$$2NiOOH + 2H_2O + Cd \overset{discharge \rightarrow}{\underset{charge}{\leftarrow}} 2Ni(OH)_2 + Cd(OH)_2$$
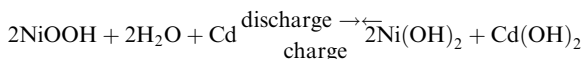
These reactions apply to the nickel/cadmium cell. In the nickel/iron cell the cadmium (Cd) is replaced by iron (Fe).
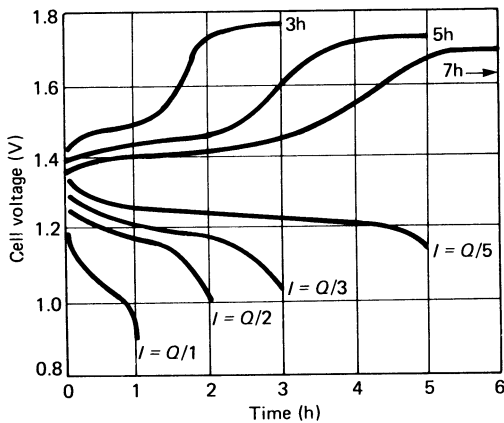
Figure 29.8   Charge and discharge characteristics of a low resistance nickel/cadmium cell

Figure 29.9   Nickel/iron cell

The electrolyte is a solution of pure potassium hydroxide (KOH) of relative density about 1.200, a small amount of lithium hydroxide being sometimes added. The electrolyte takes no apparent part in the reactions and its density remains substantially constant. Cells can stand indefinitely in any state of charge, provided that the plates are kept immersed. As in the lead/acid cell, water is lost during gassing on charge and is made up with distilled water. Electrolyte is added only to make good accidental spillage.

Typical charge and discharge characteristics are shown in *Figure 29.8*. The time for a full charge is 7 h, the voltage per cell rising from about 1.4 V at the start to about 1.8 V (nickel/iron) or 1.7 V (nickel/cadmium) after about 5½ h, and then remaining constant for the remainder of the charge. The input (in ampere-hours) should be 1.4–1.5 times as great as the previous discharge. Filler caps or vents should be kept closed except when topping up or taking gravity readings.

As alkaline cells are not damaged by overcharging, a full normal charge can be given irrespective of the state of the cells.

29.4.2.2   Construction

Nickel hydroxide forms the active material of positive plates, the form being 'tubular' for the nickel/cadmium and 'pocket' for the nickel/cadmium cell. Negative plates are of the pocket form for both: the active material is first pelleted, and the pellets then firmly enclosed in pockets of this nickel-plated steel, perforated with many minute holes. In tubular plates helically wound tubes of similar perforated material are constructed, and active material interspersed by layers of thin nickel flake is tamped into them. Groups of plates of the same polarity are bolted or welded to steel terminal pillars. Plates are kept apart by ebonite rod separators. The cell assembly is fitted into a welded sheet-steel container, the terminals being brought out through the lid in suitably insulated glands.

The construction (*Figure 29.9*) produces sturdy, robust cells, unaffected by vibration and shock. Batteries are built up by assembling cells in hardwood crates.

The need to increase the electrical conductivity of the nickel hydroxide positive active material of the alkaline cell was recognised at an early stage of its development. In the tubular plate this was done by introducing small pockets of
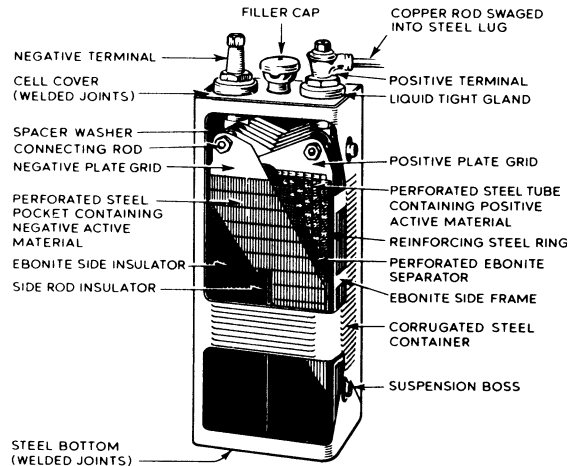
extremely thin metallic nickel flake at regular intervals in the positive active material as it was tamped into the tube. In the pocket type of plate graphite powder is mixed with nickel hydroxide before it is pressed into a pellet. The same object was achieved in a *sintered* plate developed in the late 1930s. The plate grid or support was prepared in the form of a highly porous sintered nickel plaque and the active materials (nickel hydroxide for the positive plate and cadmium hydroxide for the negative) were deposited in the fine pores from suitable solutions of their salts. In this way the active materials were distributed evenly over a very large conducting surface and relatively high coefficients of use were obtained. By this method also very thin plates could be made in closely controlled thicknesses of 0.75 mm or less, and when these were interleaved with thin separators of woven or felted cloth, close-packed assemblies were produced capable of delivering very high currents, particularly at low temperatures.

Sintered plate batteries have been extensively used in aircraft and in other applications calling for high discharge currents.

It was later discovered that if the amount of electrolyte were reduced to such a point that there appeared to be no free potassium hydroxide, the cell could be submitted to overcharge in a fully sealed condition without any risk of the container bursting. The chemistry of this reaction can be explained simply by saying that any oxygen produced at the positive electrode during charge is immediately absorbed by the cadmium in the negative electrode and this is converted to cadmium oxide. The negative charge is therefore used to reduce this cadmium oxide and no gaseous hydrogen is evolved.

Sealed cells require no topping up, evolve no vapour or spray, and can be installed in equipments without hazard. But occasionally they partially dry out, so it is the custom to fit release valves. Batteries of sealed cells have found application in aircraft.

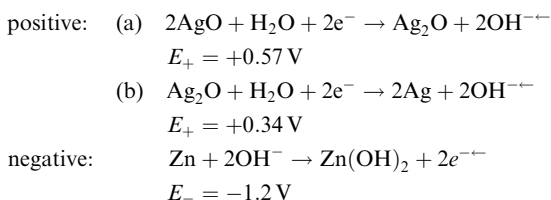Development has resulted in small cells of capacities less than 1 A-h. They are made in the form of a large button or in cylindrical shape. The former generally have compressed pellets of the active materials; the latter have thin sintered electrodes. Both have restricted amounts of electrolyte and function as fully sealed cells. They are applied to transistor radio receivers and other electronic devices.
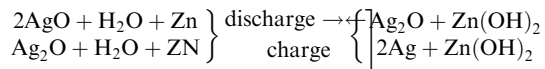
29.4.3 Silver/zinc alkaline cells

Silver/zinc alkaline cells have recently come to the fore in applications where very high outputs per unit of weight and volume are required. In these respects they give outputs from four to five times those of the equivalent lead/acid and nickel/cadmium alkaline cells. Thus, a 100 A-h cell may be only $10\,cm \times 5\,cm$ in plan and $20\,cm$ in height, and have a mass of $1.5\,kg$. The silver is costly, and in view of the relatively low reversibility of multicell batteries, silver/zinc batteries have found few commercial applications. They have been used in aircraft, in guided missiles and to supply power to the communication systems in satellites.

29.4.3.1 Charge and discharge reactions

As in the conventional alkaline system, potassium hydroxide of about 1.200 relative density is used as the electrolyte. The silver oxide used as the depolariser in the positive plate passes through two stages of oxidation (AgO and Ag_2O) each of which has a characteristic electrode potential. During discharge the following reactions take place:

positive: (a) $2AgO + H_2O + 2e^- \rightarrow Ag_2O + 2OH^{-\leftarrow}$

$E_+ = +0.57\,V$

(b) $Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^{-\leftarrow}$

$E_+ = +0.34\,V$

negative: $Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^{-\leftarrow}$

$E_- = -1.2\,V$

The overall cell reactions are therefore

$$\left.\begin{array}{l} 2AgO + H_2O + Zn \\ Ag_2O + H_2O + ZN \end{array}\right\} \begin{array}{c} \text{discharge} \rightarrow \\ \text{charge} \end{array} \left\{\begin{array}{l} Ag_2O + Zn(OH)_2 \\ 2Ag + Zn(OH)_2 \end{array}\right.$$

For the former reaction the open-circuit cell voltage is 1.81 V and for the latter it is 1.58 V.

The discharge voltage curves of silver/zinc cells therefore generally show two plateaux, a relatively short one at about 1.8 V and a relatively long one at about 1.5 V. With some pre-treatment, as, for example, a very short preliminary high-rate discharge, it is possible almost to eliminate the first plateau, and the discharge voltage then remains fairly steady at about 1.5 V per cell. A curve of this type is shown in *Figure 29.10*.

The nominal cell voltage is 1.5 V, and this is held (at normal discharge rates) substantially constant over most of the discharge period, as shown. High output currents and charge rates can be employed with little sacrifice in effective capacity. Normal ampere-hour efficiency is 90–95% and watt-hour efficiency 80–85%. Practically no gassing takes place. The electrolyte is to a major degree absorbed in the active materials and almost completely immobilised.

Owing to the slight solubility in potassium hydroxide of the higher silver oxide, overcharging of reversible silver/zinc
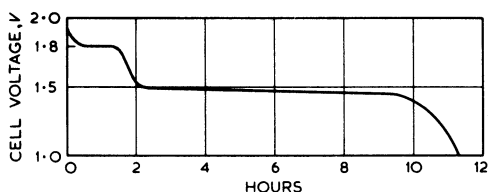

Figure 29.10 Discharge voltage of a silver/zinc alkaline cell

batteries should be avoided. In general, charging should be stopped when the voltage reaches 2.1 V per cell and, for this reason, recharging is best carried out with constant-voltage control. If this is not done, short-circuits may develop through the separators. To reduce this risk, manufacturers generally enclose the zinc negative plates in several layers of the separator material, which is usually of a cellulosic base. Single cells of this type have a fair degree of reversibility, but in a multicell battery the irregularity between cells, which is difficult to eliminate, has an adverse effect on reliability. And the greater the number of cells in the battery, the shorter the cycling life becomes.

29.4.4 Secondary battery technology

29.4.4.1 Voltage

The open-circuit voltage of a fully charged secondary cell is the same, however large or small, but varies according to the type, i.e. lead/acid or alkaline. That of a fully charged lead/acid cell is approximately 2 V; that of an alkaline cell is about 1.2 V.

Because of the difference in cell terminal voltages (2.0 V for lead/acid and 1.2 V for Ni/Cd), five Ni/Cd cells are required to replace batteries with three lead/acid cells.

29.4.4.2 Capacity

The capacity of the lead acid battery increases with decreasing rates of discharge (currents) and increasing durations (hours). It is therefore usual to state the rate of discharge for any declared capacity, e.g. at the 10-h rate, the 5-h rate, the 1-h rate and so on. *Figure 29.11* shows families of discharge- and charge-voltage curves for a typical lead/acid cell on discharge at constant current in each case. The salient properties are:

Discharge time (h)	10	7.5	5.0	3.0	2.0	1.0	0.5
Current rate (A)	11	14	19	29	40	65	118
Mean voltage (V)	2.0	2.0	1.98	1.94	1.90	1.84	1.70
Energy (A-h)	110	105	96	88	79	65	59
Power (W-h)	220	210	190	170	150	120	100

Points to note are: (a) the O/C voltage is about 2.0 V; (b) the discharge voltage curves all start with a relatively flat plateau which ends with a sharp decline, usually referred to as the 'knee' of the curve, beyond which little further capacity is available; (c) the slope of the discharge curves becomes steeper as the rate (current) increases and the knee becomes less prominent; and (d) the 'energy' capacity is represented by the product of the current and the duration (A-h) and the 'power' capacity by the product of energy and the mean voltage (W-h).

The theoretical amounts of the active materials consumed per A-h of discharge energy are: PbO_2, 4.45 g, Pb, 3.86 g and H_2SO_4, 3.68 g. The actual amounts are considerably greater as the coefficients of use fall very much below 100%, as indicated below:

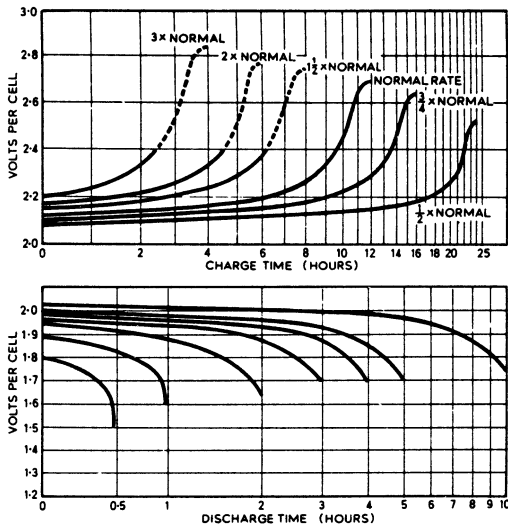|	5-h rate	1-h rate	5-min rate
Positive, PbO_2	52%	33%	16%
Negative, Pb	66%	40%	19%

Figure 29.11   Representative curves of charge and discharge

The capacity is related to the amounts of the active materials and to their porosity and intrinsic surface area. The main product of the discharge in both positive and negative active materials is lead sulphate. This has a very high electrical resistivity. It polarises the active material and, by clogging the pores restricts diffusion of the electrolyte into the reaction zones. Planté positive grids are cast with a developed area at least 10 times the superficial area and the anodically prepared active material—PbO_2 is spread in a thin layer over a large area. In Faure pasted plates on the other hand, the porosity of the active material must be adequate to permit rapid diffusion of the sulphuric acid electrolyte, particularly during discharges at high rates.

Thus, it is found that (a) for stationary batteries of the lead/acid type, on the score of durability and efficiency it is best to use a Planté positive with a large surface area lightly coated with active material; (b) for automobile or diesel engine starter batteries it is best to use a large number of comparatively thin pasted plates; and (c) for traction battery service, where lower rates are usual, thicker plates with denser material can be used.

29.4.4.3   Charging

All secondary batteries require a supply of direct current for recharging. The method of charging is important in its effect on battery performance and service life. The three principal methods are as follows.

System control   The batteries work in parallel with a generator across the load. Typical applications include motor vehicles, in which the battery forms an essential standstill reserve for ignition, lighting, signalling, etc. Most small motor cars employ a d.c. generator with control gear for cutting out the generator when its speed is too low, and for voltage regulation for operation over the wide range of active speed. Larger cars and road vehicles employ a.c. generators (alternators) with rectifiers and appropriate automatic control equipment.

Manual or semi-automatic control   Here the battery is recharged from a separate source, such as a transformer/
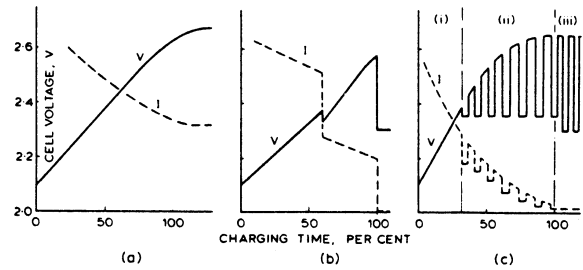

Figure 29.12   Charger waveforms

rectifier. Typical applications are to electric vehicles, in some cases with the transformer/rectifier carried on the vehicle.

Since the performance and life of motive power batteries largely depend on the efficiency of the charging system, these will be described in more detail. Three forms of charger are in general use, the single-step taper charger, the two-step taper charger and the pulse-control charger, of which the Chloride Spegel is a typical example. The voltage-current-time relationships for these three types are shown in *Figure 29.12*. With the single step charger, the voltage is held constant just below the battery gassing point, 2.4 V per cell. When the battery voltage reaches this point, the current is allowed to decay until the battery becomes fully charged. With the two step process, the first stage follows the same line as with the single step; the current is then reduced to a pre-determined value and charging continued for a pre-determined period. The pulse type of charger is devised more to keep the battery fully charged. When the main charge is stopped, the battery receives short pulses of charge, controlled by the decay in the battery voltage during the intervening open-circuit period.

Float-and-trickle control   Large stationary batteries in generating stations and (for emergency lighting) in hospitals are connected permanently to a charger, and may also be connected across the load. In normal operation the battery receives a trickle charge to keep it fully charged and ready for intermittent loading. Such a battery requires ventilation and ready access for servicing.

29.4.4.4   Maintenance-free, gas recombination technology

One of the most important developments in storage batteries during the past 20 years or so has been the production of maintenance-free (MF) systems. The primary object was to reduce or eliminate altogether the need to replace water lost through three main factors; (a) evaporation; (b) local electrochemical action at lead negative plates due to the deposition of metals, such as antimony having a lower hydrogen overvoltage than lead; and (c) electrolysis of the aqueous electrolyte towards the end of each recharge. With well-stoppered cells, (a) presented few problems. So far as (b) was concerned, from the earliest days of manufacture, antimony has been the favourite hardener for the lead grids used to support the active materials and to collect the current. But, because of their different hydrogen overvoltages, when lead and antimony come in contact in the electrolyte, hydrogen is evolved, water in the electrolyte is decomposed, some of the lead active material is oxidised causing a corresponding loss of capacity—the so-called 'standing loss'. Many metals have been tested in lead alloys for this application

and the most successful has been lead–calcium alloy, containing 0.08% calcium and small amounts of tin. With grids cast in this metal, standing losses are negligible. Losses by the third factor (c) proved more difficult to contain, but following the route taken for alkaline cells, the principle of gas re-combination has now been fully established for lead–acid batteries. The main requirements are: (a) no free electrolyte (to permit rapid diffusion of oxygen to the negative plate surfaces, the elements should be 'starved' of electrolyte); (b) the bulk of the electrolyte should be retained by the porous separators; and (c) there should be excess negative capacity. Oxygen is evolved from the positive group before the negative is fully charged. It diffuses to the negative plates where it is absorbed causing discharge of the active material. The negative plates are, therefore, never fully charged and hydrogen is not evolved. This principle is now being applied to cells of various types from small button cells to batteries for SLI, traction and stationary service. Cells can be fully sealed, though it is usual to incorporate a pressure-controlled safety valve.

29.4.5 Lithium cells

In recent years there has been much activity on the part of the battery companies directed towards developing cells having lithium electrodes. These electrodes have many potential advantages in battery technology, including high cell voltages, high energy densities, high power densities and rechargeability. Thus they give rise to both primary and secondary batteries. Lithium as an electrode gives a high energy/mass ratio and an inherently high power density. The standard electrode potential is over $-3.0\,V$ and when allied with, say, a fluorine electrode ($E_0 = +2.87\,V$), the resulting cell should theoretically have an O/C voltage of over $6.0\,V$. However, problems arise in practice because of the extreme reactivity of lithium which is stable only in certain non-aqueous media (see below) and even in these it is often the formation of surface films on the lithium which determines the performance of the battery.

There are many different types of lithium cell, having both different electrolyte solutions and different positive electrodes, but with a common lithium negative electrode. The solvents include organic materials such as propylene carbonate containing lithium salts, inorganic materials such as thionyl chloride, molten salts such as the lithium chloride/potassium chloride eutectic and solid electrolytes such as lithium iodide and organic polymers, e.g. polyethylene oxide.

Lithium/thionyl chloride battery technology is both well advanced and well established. Notable features of these batteries are their very flat discharge characteristics, long shelf-life and applicability over wide temperature ranges.

Although a wide range of primary lithium batteries are now commercially available it has not been straightforward to produce viable secondary cells. The problems mainly arise in subjecting both the negative and positive electrodes to charge/discharge cycles in these cells.

The following couples have been employed with organic electrolytes: Li/MnO_2, Li/SO_2, $Li/(CF)_n$, Li/MoS_2, Li/Ag_2CrO_4, Li/CuO, Li/FeS_2 and Li/TiS_2. Unfortunately, the electrical resistance of these organic electrolytes, even when improved by inorganic salt additives, is relatively high and cells of this type are only suitable for low rate discharges.

With molten LiCl–KCl, the alloys Li–Al and Li–Si have been used as negative electrodes, and FeS and FeS_2 as positive electrodes. Operational temperatures may be as high as $400°C$.

The Li/SO_2 and $Li/SOCl_2$ couples have inorganic electrolyte and can be operated at high discharge rates at ambient temperatures. They have, in fact been tested for possible torpedo propulsion.

29.4.6 Sodium/sulphur cells

Another high-temperature contender ($300/375°C$) is the sodium/sulphur cell, which employs liquid sodium and sulphur as the negative and positive electrodes, respectively, with the solid electrolyte β-alumina which is a sodium ion (Na^+) conductor. It is envisaged that this system would be used for load levelling and car traction. The open circuit voltage of a single cell is 2.1 V and its theoretical energy density 756 W-h/kg. Safety is a major concern. In practice, cells have capacities of about 150 A-h with practical energy densities in the 100–150 W-h/kg range. Heat management is also very important; it is desirable to employ the batteries for applications which enable them to remain molten during on and off periods. In the UK a company (Chloride Silent Power) set up by the Electricity Council and the Chloride Group is exploiting the sodium/sulphur battery for large-scale application.

29.5 Battery applications

29.5.1 Stationary or standby power batteries

Batteries in large installations having capacities of hundreds of ampere-hours, which supply power in emergency or auxiliary situations, are referred to as stationary or standby batteries. Standby power supply is needed when the mains source of electricity fails. The choice of standby supply is usually between lead–acid or nickel–cadmium batteries or auxiliary generators, or a combination of both sources. Applications include emergency lighting in department stores, offices, factories, cinemas and other public places, power to keep burglar alarms and other communications working, emergency power for important production processes and equipment such as in hospitals, mines, airports, power stations, telephone exchanges, lighthouses and, more recently, computer operations especially in the financial service sector.

29.5.1.1 Lead–acid batteries

Various types of lead–acid secondary batteries are used for stationary or standby purposes:

● Plante cells giving a long life of 20–35 years or even longer with high reliability which are kept on continuous trickle charge. Cell capacities are rated by relating current flow to time in ampere-hours. High performance cells up to 2000 Ah are usually in transparent containers allowing acid levels to be checked.
● Flat plate cells provide a cheaper but short-lived alternative to Plante cells. Pasted flat plate cells, again in transparent containers are available in capacities of up to 500 Ah with a life expectancy of 10–12 years to meet emergency lighting regulations. Car batteries are based on this design but are totally unsuitable as an emergency power source being designed instead to give a high current for a short time.
● Tubular cells are normally used to power electric trucks on which daily recharging is needed, but are suitable for standby applications requiring frequent charge/discharge cycles. When on standby they have a life expectancy of 10–12 years compared to 5 years when powering electric trucks.

29.5.1.2 *Nickel–cadmium batteries*

Large nickel–cadmium secondary batteries, open and semi-open or sealed are made in a variety of designs to meet many purposes including those of stationary or standby batteries. Their uses cover the application areas mentioned above. Other applications include engine starting for motor-generating sets as required for standby power systems where bad weather, low temperature conditions might prevail. Under these circumstances engine-starting batteries must be highly reliable, have a high performance capability and be free from the effects of high stress and vibration, such as occurs in vehicles or engine rooms of ships. A similar requirement is for emergency batteries in trains for lighting at stations or in the case of a power supply failure. Nickel–cadmium cells are used also for the uninterrupted emergency power supply (UPS) to railway mainline stations and signalling systems. Marine applications include UPS systems for radar, communications, steering and navigation and for the emergency lighting on board. In air transport these batteries provide ground power supplies, the support battery systems on board aircraft and at airports all the essential lighting and communications depend on batteries. UPS systems operate in standby mode, providing power only in the event of mains failure.

29.5.2 Self-contained power supplies

Applications as self-contained power supplies include a wide range of portable devices such as transceivers, razors, portable equipment and tools, radios, torches, toys, hearing aids, cameras, calculators, computers, clocks, etc.

Sealed nickel–cadmium secondary batteries have a range of uses in these markets resulting from their favourable characteristics including:

(1) total absence of maintenance;
(2) very long operational life;
(3) ability to accept permanent overcharge;
(4) prolonged storage without deterioration;
(5) ability to be overcharged at high rates;
(6) constant discharge voltage characteristic;
(7) mechanically robust; and
(8) operation over a wide temperature range of $-40°C$ to $+50°C$.

If the application requires a low initial cost, or the life of the equipment is short, however, then primary batteries are the obvious choice. Secondary batteries can prove cheaper in the long run because they can be recharged and reused, but they require a charger, so the initial cost of the battery system is high.

Of the primary cells zinc–carbon is cheap and readily available. It is particularly useful in applications having a light, intermittent duty cycle, but the battery has a low shelf life and a drooping discharge characteristic. For heavy-duty applications needing continuous operation at high current, alkaline manganese dioxide batteries are preferred to zinc–carbon. They have 50–100% more energy for the same weight and a longer shelf life, but are more expensive at low currents, e.g. below 200 mA. The mercury-oxide battery has a flat discharge characteristic and a high energy to weight ratio. It is often used in voltage reference applications. Lithium batteries are used in applications that require a long shelf life or a wide operating temperature range, or a high energy density.

29.5.3 Traction batteries

Much of the recent interest in battery development has been linked to traction purposes. There have been a number of obstacles to the widespread introduction of electric vehicles (EVs) based on batteries alone:

● Inability to store sufficient energy for long distance travel;
● Time taken to recharge the battery;
● Lack of supporting infrastructure of fore-court services and maintenance facilities;
● Replacement costs of battery pack; and
● Additional vehicle weight of battery pack.

Lead–acid and nickel–cadmium store too little energy per unit weight and volume to be viable for electric traction; therefore the development of the electric vehicle is critically dependent on designing advanced batteries which can store two to three times the amount of energy per unit weight and volume compared with these conventional rechargeable batteries. Significant advances have been made in electrochemical battery development, however, over traditional lead–acid battery performance. Advanced battery technologies such as room temperature lithium ion and high temperature sodium nickel chloride have energy densities of 2.5 to 3 times that of lead acid, resulting in electric vehicle ranges of possibly 150–250 km at 100 km/h, i.e. suburban use, with sufficient energy to power normal levels of auxiliary equipment. The high temperature sodium nickel chloride battery (sodium metal negative electrode—nickel chloride positive electrode separated by an ion conducting β-alumna ceramic) is a robust technology with demonstrated cycle life, performs well in cold weather, but would not be energy efficient in vehicles with low mileage because of the self discharge needed to keep the battery heated. The lithium ion battery has good energy performance, is safe, but has relatively low specific power and requires considerably more development; nevertheless the development of high-power systems are anticipated in the future.

The state of development of secondary batteries along with the targets set by electric passenger vehicle (EV) requirements is summarised in *Table 29.1*. The data does not account for improvements which can be made by properly designed engine-management systems. The use of ultracapacitors, for example, can supplement power supplied. A battery's life could be as much as doubled by the use of ultracapacitors for load-levelling purposes. This technology is well suited for delivering high power to EV's during acceleration and generating new energy supply during braking using power electronics for four-quadrant control.

29.6 Anodising

Anodising is the production of a film of oxide or hydrated oxide on the surface of aluminium or of its alloys, to prevent corrosion of aircraft metal and other surfaces likely to be exposed to the effects of the sea. The anodic film is usually of a light grey colour. When newly formed, it can absorb dye, a property of use for decorative purposes.

29.6.1 Process

The workpiece is made the anode in a bath of chromic or sulphuric acid, through which a direct current is passed at a voltage of about 50 V for the former acid bath and 10 V for the latter. In large installations a current of 1–2 kA may be required from a rectified a.c. supply. The action produces on the aluminium workpiece a semi-insulating film, and

Table 29.1 Battery performances and traction requirements

Cost £/kWh	Required performance	Present achievements
Lead–Acid	75–100	50–100
Nickel–Iron		100–200
Nickel–Cadmium		150–200
Nickel–Metal hydride		100–150
Sodium–Sulphur		100–200
Sodium–Nickel chloride		200–300
Lithium polymer		25–250
Specific power W/kg		
Modern car engine		400
Lead–Acid	300–400	67–183
Nickel–Iron		70–140
Nickel–Cadmium		100–200
Nickel–Metal hydride		150–200
Sodium–Sulphur		90–130
Sodium–Nickel chloride		100–150
Lithium polymer		75–100
Specific energy Wh/kg		
Modern car engine		200
Lead–Acid	100–200	18–56
Nickel–Iron		40–70
Nickel–Cadmium		33–70
Nickel–Metal hydride		54–80
Sodium–Sulphur		80–140
Sodium–Nickel chloride		75–100
Lithium Polymer		125–150
Energy density Wh/litre		
Lead–Acid	150–300	50–80
Nickel–Iron		60–120
Nickel–Cadmium		60–120
Nickel–Metal Hydride		150–200
Sodium–Sulphur		75–125
Sodium–Nickel Chloride		125–175
Lithium Polymer		100–120
Life–years		
Lead–Acid	5–10	2–3
Nickel–Iron		3–5
Nickel–Cadmium		?
Nickel–Metal Hydride		5–10
Sodium–Sulphur		?
Sodium–Nickel Chloride		3–5
Lithium Polymer		?
Number of Discharge cycles		
Lead–Acid	500–1000	500–1000
Nickel–Iron		500–2000
Nickel–Cadmium		1500–2000
Nickel–Metal Hydride		750–1000
Sodium–Sulphur		250–750
Sodium–Nickel Chloride		500–750
Lithium Polymer		250–500

the vat voltage is increased as the action proceeds. Non-aluminium parts must be screened by plastics materials. The current density is 0.5–$0.7\,A/cm^2$ of active anode surface. In a typical process about 10 V is initially applied, the current being 1.5 kA; after 30 min the voltage is steadily raised in 5 min to 50 V, and maintained for a further 5 min. The work is then removed from the vat and washed.

The liquid carries the anodising process into every bare recess so long as there is no exclusion by gas. A tube 2 m long and of 5 mm internal diameter can be satisfactorily anodised over its entire surface. The effectiveness of the surface can be tested by applying 50 V between the workpiece and a 25 mm diameter steel ball. Anodising is best carried out at a standard temperature (e.g. $40°$C).

29.6.2 Vats

In small baths the cathodes are carbon plates or rods hung from the cathode connection. Current is conveyed to the cathodes and the anode workpiece by round copper rods resting on porcelain insulators attached to the rim of the wooden or metal vat. A typical vat is $6\,m \times 2\,m$ with a depth of about $2\,m$, sunk into a concrete floor for convenient access. The cost of filling a bath with diluted acid is considerable, making necessary scrupulous attention to cleanliness and the avoidance of contamination. Precipitates must be allowed to settle or be filtered off. Gentle agitation of the liquid by means of compressed air from a small motor-driven pump is applied to avoid slight pitting of the workpiece at the liquid surface level: this keeps foreign bodies in suspension, so that filtering may be necessary at the end of the day's work.

29.6.3 Workpieces

The pieces to be anodised are wired for connection to the anode rod by aluminium wire if they are small. Larger pieces may be connected by dural rods and clamps. The cross-section of the wires and rods must be adequate for the appropriate current, and that of the connection point to the workpiece must also be sufficient. Multiple connections can be used for this purpose. The action of the bath produces an effervescence of oxygen from the aluminium and dural, and a gas accumulation may exclude workpiece recesses from the anodising process. This can be overcome by tilting the workpiece, or may necessitate two runs with the workpiece in different orientation.

29.6.3.1 Cleaning

Before anodising, workpieces must be cleaned by a process similar to those for the preparation of work for electroplating. Items that have not been heat-treated, welded or riveted are more easily cleaned than fabricated parts or castings. If the workpiece has been previously treated in a salt bath, all trace of the salt must be removed by flushing in running water. Built-up fittings require the joining surfaces to be scratch-brushed or buffed before refitting, and immersed in boiling water immediately prior to anodising. Welded aluminium parts must be kept in contact with boiling water for 30 min to remove flux residues, which lead to pitting. In large anodising shops greasy articles are held in the smoke arising from electrically heated trichloroethylene, which cleans them thoroughly in about $2\,min$. Before anodising they are dipped in a hot swill to remove traces of the smoke, which would contaminate the anodising bath.

29.7 Electrodeposition

Electrodeposition is carried out in electrochemical reactors that use electrical energy to extract metals from their compounds. The processes include electrowinning, electrorefining, electroplating and electroforming.

Electrowinning A mineral, or a compound prepared therefrom, is decomposed to a metal and (usually) a gas. The prime process in this class is the refining of aluminium: the Hall–Heroult process involves the electrolytic decomposition of alumina (prepared from bauxite) dissolved in molten cryolite (Na_3AlF_6) at about $1000°C$. Aluminium is produced as a liquid at the cathode. The primary anode product, oxygen, reacts with the carbon anode to give mainly carbon dioxide, with a small proportion of carbon monoxide. The process is highly energy intensive.

Electrorefining An impure anode (perhaps a cathode from an electrowinning stage) is converted to a pure cathode. Copper is refined in this way. The process is much less energy intensive than electrowinning, mainly because of the lower voltages employed.

Electroplating This is the electrodeposition of a thin protective metal coating on another metal. Protection is obtained with the minimum amount of material and with a low expenditure of energy. The process has imperfections: for example, chromium plating has high porosity and poor adherence, particularly in extreme conditions.

Electroforming The aim in this extension of electroplating is to build up the plate so that the cheap substrate can be dissolved to leave an article of the plate metal which has mechanical integrity. Nickel electroforms are made in this way, but the process is particularly advantageous for refractory metals (e.g. tantalum, niobium). Thus, an article that would be costly and wasteful when made from bulk metal can be prepared directly.

29.7.1 Electroplating

In modern mass production processes automatic plating plants are regularly used for the deposition of nickel, chromium, brass, zinc, silver, copper and cadmium, and, in addition, for depositing composite coats of two metals, such as in nickel and silver plating, brassing and bronzing. In using plants of this kind, the product is extremely consistent, as the plater is relieved from manual duties and left free to devote his attention to the control of essential operations. The plant is usually arranged so that the various vats are placed in line one behind the other in proper sequence. Two conveyors travel slowly over the vats, the articles to be plated being loaded on insulated suspenders which are arranged in two or three rows on cross rods attached to the conveyor chains. The suspended articles pass in succession through cleaning and swilling vats before passing to the vats for deposition, and finally to the swilling and drying-out apparatus after plating is completed.

As each loaded cross rod arrives at a vat or tank it is lifted by an auxiliary fast-moving transfer chain, and lowered into the next vat along the line. After passing through drying apparatus, the suspenders are unloaded from the cross rods, the latter being automatically returned to the loading position for the work to continue. The cycle of operations in the case of automatic nickel-plating plants is usually as follows: hot alkaline electrolytic cleaner used cathodically at about $300\,A/m^2$; cold water swill; anodic etch in sulphuric acid in the case of iron and steel articles; agitated cold water swill; nickel plating; cold water swill; hot water swill; and drying.

29.7.1.1 Barrel plating

The barrel planting method of electroplating is automatic insofar as the actual deposition of metal is concerned, and the method is extremely efficient and economical within the limits of the capacity of the barrel and the size of the articles. Any difficulties experienced are usually traceable to overloading the barrel, which causes the articles to be carried round in a mass as the barrel revolves, or to attempts to plate articles having awkward shapes which shield one another in the mass and prevent regular deposition.

Plating barrels are available for use with all types of solutions, and excellent results can be obtained with such articles as screws, cycle and car fittings, and hooks and eyes. Some of the early machines were extremely clumsy, and offered great resistance to the flow of current, since when many improvements have been made, particularly in the use of rubber lined tanks, stoneware vats and containers of other non-metallic material.

An important advantage of barrel plating is that, as the articles are receiving the deposit of metal, they rub together and become burnished, while the deposit being consolidated by the rubbing is close-grained and durable. As in so many plating processes, the speed at which a plating barrel should revolve is critical and is governed by the class of article being plated and the diameter of the barrel.

Speeds vary between 30 and 45 rev/min, although in the case of large plating barrels the speeds may be as low as 10–15 rev/min. It sometimes happens that articles all of one shape cannot conveniently be plated in a barrel by themselves, and in such cases scrap metal pieces or steel balls of suitable size can also be put into the barrel.

Although barrel plating can be carried out with some solutions at 6 V, it is usually necessary to use voltages of 10–18 V. In the case of nickel a current of about 45–60 A at 10 V can be passed. A higher current is needed for 'brassing'.

Barrel plating was developed specially for handling small articles in quantities, and in many cases this process has a number of advantages over the original suspended anode method. In one of the best-known makes the anode insulated by a vulcanite cover is situated at the base of the barrel. The barrel itself is made of welded steel internally lined with vulcanite, and is mounted on a swivel arrangement, which permits immediate removal of the work by dumping it into a suitable container for transfer to the drier. Electrical contact is made through an insulated rod passing through the centre of the shaft and directly connected to the anode, the current returning to the plating rectifier by way of the barrel and framework of the machines. An important feature of this type of barrel is that it can be relined with vulcanite at very small cost, and it is also easily and quickly rinsed.

29.7.1.2 Polishing

The speed of a polishing mop or bob is a factor affecting efficiency and economy, and speeds between 30 and 45 m/s are the rule according to the article to be polished.

Variable-speed machines are necessary, so that when a mop or bob becomes worn, say from 30 to 20 cm in diameter, the peripheral speed may be increased. Too low a speed causes a mop to drag and the articles to become heated, and a burnishing rather than a polishing effect is produced. 'Polishing bobs' is the term used for all solid leather wheels, compress wheels, made up of sections of leather, canvas or felt, and solid felt. These are dressed with emery, and the felt bob is the type in most general use. Polishing mops consist of discs of cotton cloth, varying in size from 5 to 40 cm in diameter and held together at the centre by means of washers of leather or fibre.

29.8 Hydrogen and oxygen electrolysis

There are several processes by which oxygen and hydrogen are produced as a main product or by-product. The industrial uses are considerable.

Oxygen   is used to a very large extent in metal working and metallurgical industries. In conjunction with acetylene or hydrogen, it is used for welding and cutting; with butane and propane, for tempering steel. Very large (tonnage) quantities are now used in the production of steel, in the gasification of coal and to a lesser extent in the oxidation of olefines. The use for medical purposes and in super-atmospheric aviation is relatively small in quantity but of high importance.

In the chemical industry oxygen or oxygen enriched air is sometimes used in place of air in the oxidation of ammonia to produce nitric acid in highly concentrated form. The electrolysis of water can therefore conveniently be used for the production of hydrogen for the synthesis of ammonia and of oxygen for the subsequent preparation of nitric acid. The nitric acid and ammonia together produce ammonium nitrate, an important fertiliser.

Hydrogen   is used in a number of industries. In the food industry the production of margarine and cooking fats from liquid oils such as groundnut, cottonseed, whale, etc., is based upon the partial catalytic hydrogenation of these oils, which converts them into solids at normal temperatures. Sorbitol, a sugar used by diabetics and in the production of synthetic resins, is produced from glucose by hydrogenation. Ammonia, a basic chemical for the fertiliser industry, is produced in very large quantities annually by the catalytic combination under high pressure of hydrogen and nitrogen.

Large quantities are used in the fuel industries, mainly in the processing of mineral oils but also in the production of synthetic liquid fuels from coal.

Many other uses exist in the chemical industry, such as in the production of synthetic solvents and the hydrofining of benzole. In the metallurgical industry hydrogen alone or mixed with nitrogen is used to provide inert atmospheres for the annealing of alloy steels, and in the lamp industry it is used for the reduction of tungsten and molybdenum ores to the metals and in the subsequent manufacturing processes for the production of lamps. Large synchronous machines are sometimes cooled by the circulation of hydrogen in a closed system. Meteorological balloons are filled with the gas.

29.8.1 Process

Water dissociation to give small (equal) concentrations of the hydronium ion (H_3O^+) and the hydroxide ion (OH^-) is in accordance with the equation

$$2H_2O \rightarrow H_3O^+ + (OH)^-$$
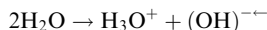
Thus, it is possible in principle to decompose water electrolytically in an electrochemical reactor, to give hydrogen at the cathode and oxygen at the anode according to the reactions

cathode: $2H_3O^+ + 2e^- \rightarrow H_2 + H_2O$

anode: $4(OH)^- \rightarrow 2H_2O + O_2 + 4e^-$
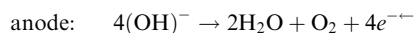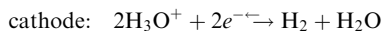
Practical reactions are slightly more complex, as the electrolyte added to the water to improve its conductivity plays a role in the reaction.

In simple water electrolysis the hydrogen produced per coulomb is 0.010 45 mg/C. Thus, 1 kA produces 0.42 m^3/h (at 0°C, 760 mmHg, dry). The corresponding quantity of oxygen is 0.21 m^3/h. Stray current prevents full attainment of these outputs, but the current efficiency can be as high as 98–99%. The specific energy consumption depends on the voltage. The decomposition voltage of water is 1.23 V, but that to operate a hydrogen/oxygen cell exceeds this value, because of the ohmic resistance of the electrolyte and the overpotentials for the evolution of the gases at the electrodes. Solutions of caustic soda or potash are almost

invariably used to lower the resistivity, using mild steel cathodes and nickel-plated anodes, which are immune to attack by the electrolyte or the gases. Soda and potash solutions are always prepared from the purest material: the caustic must have limited amounts of chlorides, sulphates and carbonates, which raise the resistance, while the former two may cause corrosion of the electrodes. The water feed must be pure (i.e. a very high resistivity). It is produced in a water still or by treating the raw water in an ion exchange plant, followed sometimes by active carbon treatment to remove oil traces, as when the source is a steam condensate.

29.8.2 Electrolysers

Water electrolysers are distinguished by electrode arrangement and gas pressure.

29.8.2.1 Tank type

The tank or unit-cell electrolyser has unipolar electrodes in one tank and connected in parallel. Normally several tanks are connected in series, facilitating extension and enabling a faulty tank to be bypassed.

29.8.2.2 Filter-press type

The filter-press type has bipolar electrodes arranged to act as a positive on one side and a negative on the other, with terminal connections at the end of the battery. *Figure 29.13* shows a section, the construction having some similarity to a filter press. The cell frames (1) are made of an electrically insulating caustic-resistant material and into them are fitted the diaphragms (9) and main electrodes (10). In order to maintain the optimum distance between the active faces of the electrodes, the main electrodes each carry a perforated auxiliary cathode (11) and a similar auxiliary anode (12). The various ports are sealed off from one another, and the whole assembly of a number of cells is made leak proof by means of the joints (2). The action is as follows.

Hydrogen evolved at the cathode (11) rises through the gas port (5), carrying with it some of the electrolyte. The mixture passes along the channel (4) common to the pack of cells, thence to an arrangement of gas washing and cooling drums mounted on the electrolyser, from which the gas passes to process. The electrolyte, after cooling, returns by a pipe system through a filter to the electrolyte channel (7).
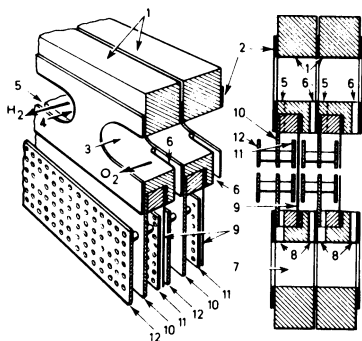

Figure 29.13 Section through a typical 'filter-press' electrolyser. 1, cell frame; 2, joint; 3, oxygen gas channel; 4, hydrogen gas channel; 5, hydrogen gas port; 6, oxygen gas port; 7, electrolyte channel; 8, electrolyte ports; 9, diaphragm; 10, main electrode; 11, auxiliary cathode; 12, auxiliary anode

The ports (8) then ensure an electrolyte feed to each cell to replace that taken out with the gas. A similar circulation occurs with the oxygen from the anodes (12) through the ports (6) and channel (3) returning through (7) and (8). The current connections to the electrolyser are to the electrodes at the ends of the pack, which are extended beyond the bottoms of their respective cells for cable or bus-bar.

It will be seen that, for a given output, a filter press electrolyser is constructed as one unit consisting of a number of cells of an appropriate size, clamped together as a pack, variations in the size and number of electrodes being made to suit the required electrical conditions. A tank type electrolyser, on the other hand, will consist of a number of unit cells connected in series externally, but here again variations in size and number can be made to suit the electrical conditions.

The filter-press electrolyser can produce in a single unit up to $500\,\text{m}^3/\text{h}$ of hydrogen: the connections are simple; gases can be delivered at normal gas holder pressures without the need for separate boosters; the electrolyte is in an enclosed system and the constant circulation through a filter ensures thorough mixing and freedom from contamination; and the quantity of electrolyte is small compared with the output.

29.8.2.3 Pressure type

The pressure type electrolyser is a development of the filter-press electrolyser in which electrolysis is carried out under pressure. Lower cell voltages are obtained because of decreased blanketing effect of the smaller gas bubbles. The optimum pressure is about 30 atm, giving a 14% power advantage over that achieved at normal atmospheric pressure. Further, the cost of post-compression of the gases is less. The basic design is similar to that of the filter-press type, but adapted to work under pressure, having cells of circular section. Gas purity is a little less than for the unpressurised equipment, but is adequate for most industrial purposes.

29.8.3 Gas purity

The makers of atmospheric pressure filter-press electrolysers guarantee a purity of 99.7% for oxygen and 99.9% for hydrogen. A check is normally kept on the gas purities by drawing off samples into measuring burettes. In the case of oxygen the sample is then passed over copper, which combines with the oxygen and leaves the hydrogen impurity as residue; while in the case of hydrogen, a platinum spiral electrically heated to redness in the gas causes the oxygen impurity to be removed by a combination with twice its volume of hydrogen to form water, leaving the main bulk of hydrogen as residue.

Automatic gas analysers can also be fitted which give a continuous check on gas purities.

29.8.4 Plant arrangement

The electrolytic plant will usually comprise a source of direct current, the electrolyser, a tank for the storage and make-up of electrolyte and a transfer pump, a source of purified water, gas holders and compressors for hydrogen and oxygen, and pressure storage tanks. In the case of pressure electrolysers buffer tanks are provided in place of low-pressure gas holders. The direct connection of electrolysers working at low pressure to compressors is not recommended.

Depending on the required specification of the gases, dryers are installed before the gases are delivered to process. The capacities of gas holders, compressors and high-pressure storage vessels depend upon the user process and its demand cycle. The compressors are normally started and stopped automatically by pressure switches on the high-pressure storage vessels and capacity switches on the gas holders. Complete automatic control of electrolytic plants including variation of output to suit demand is possible but so far has not been attempted.

Because of the explosion hazard, electrolysers are housed in rooms isolated from the electrical conversion equipment by a gasproof wall, intercommunication between the two being by outside doors. Lighting of the electrolyser room can be either by pressurised fittings or by lamps placed outside the windows.

The electrical energy consumption for the production of given quantities of hydrogen and oxygen depends on the type of electrolyser and on the output per unit cell, because the cell voltage increases with the current density at the electrodes. For atmospheric types the operating voltage per cell is 1.9–2.1, corresponding to specific d.c. energy consumptions of 4.5–5.0 kW-h/m^3 of hydrogen. The selection of an electrolyser for a given duty is based on the capital cost of the installation and the cost of energy. Thus, where the energy cost is low, it is economic to work at a high current density (and therefore a high specific energy consumption).

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