Batteries

Vehicle batteries

Requirements of the vehicle battery

The vehicle battery is used as a source of energy in the vehicle when the engine, and hence the alternator, is not running. The battery has a number of requirements, which are listed below broadly in order of importance.

- To provide power storage and be able to supply it quickly enough to operate the vehicle starter motor.
- To allow the use of parking lights for a reasonable time.
- To allow operation of accessories when the engine is not running.
- To act as a swamp to damp out fluctuations of system voltage.
- To allow dynamic memory and alarm systems to remain active when the vehicle is left for a period of time.

The first two of the above list are arguably the most important and form a major part of the criteria used to determine the most suitable battery for a given application. The lead-acid battery, in various similar forms, has to date proved to be the most suitable choice for vehicle use. This is particularly so when the cost of the battery is taken into account.

The final requirement of the vehicle battery is that it must be able to carry out all the above listed functions over a wide temperature range. This can be in the region of -30 to $+70\,^{\circ}$C. This is intended to cover very cold starting conditions as well as potentially high under-bonnet temperatures.

Choosing the correct battery

The correct battery depends, in the main, on just two conditions.

1. The ability to power the starter to enable minimum starting speed under very cold conditions.

2. The expected use of the battery for running accessories when the engine is not running.

The first of these two criteria is usually the deciding factor. Figure 3.1 shows a graph comparing the power required by the starter and the power available from the battery, plotted against temperature. The point at which the lines cross is the cold start limit of the system (see also the chapter on starting systems). European standards generally use the figure of $-18\,^{\circ}$C as the cold start limit and a battery to meet this requirement is selected.

Research has shown that under 'normal' cold operating conditions in the UK, most vehicle batteries are on average only 80% charged. Many manufacturers choose a battery for a vehicle that will supply the required cold cranking current when in the 80% charged condition at $-7\,^{\circ}$C.

Positioning the vehicle battery

Several basic points should be considered when choosing the location for the vehicle battery:

- Weight distribution of vehicle components.
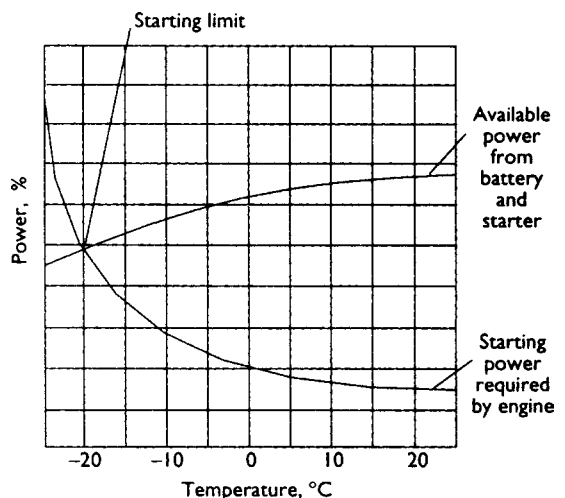- Proximity to the starter to reduce cable length.

Figure 3.1 Comparison of the power required by the starter and the power available from the battery plotted against temperature

- Accessibility.
- Protection against contamination.
- Ambient temperature.
- Vibration protection.

As usual, these issues will vary with the type of vehicle, intended use, average operating temperature and so on. Extreme temperature conditions may require either a battery heater or a cooling fan. The potential build-up of gases from the battery may also be a consideration.

Lead-acid batteries

Construction

Even after well over 100 years of development and much promising research into other techniques of energy storage, the lead-acid battery is still the best choice for motor vehicle use. This is particularly so when cost and energy density are taken into account.

Incremental changes over the years have made the sealed and maintenance-free battery now in common use very reliable and long lasting. This may not always appear to be the case to some end-users, but note that quality is often related to the price the customer pays. Many bottom-of-the-range cheap batteries, with a 12 month guarantee, will last for 13 months!

The basic construction of a nominal 12 V lead-acid battery consists of six cells connected in series. Each cell, producing about 2 V, is housed in an individual compartment within a polypropylene, or similar, case. Figure 3.2 shows a cut-away battery showing the main component parts. The active material is held in grids or baskets to form the positive and negative plates. Separators made from a microporous plastic insulate these plates from each other.

The grids, connecting strips and the battery posts are made from a lead alloy. For many years this was lead antimony (PbSb) but this has now been largely replaced by lead calcium (PbCa). The newer materials cause less gassing of the electrolyte when the battery is fully charged. This has been one of the main reasons why sealed batteries became feasible, as water loss is considerably reduced.

However, even modern batteries described as sealed do still have a small vent to stop the pressure build-up due to the very small amount of gassing. A further requirement of sealed batteries is accurate control of charging voltage.

Battery rating

In simple terms, the characteristics or rating of a particular battery are determined by how much current it can produce and how long it can sustain this current.

The rate at which a battery can produce current is determined by the speed of the chemical reaction. This in turn is determined by a number of factors:

- Surface area of the plates.
- Temperature.
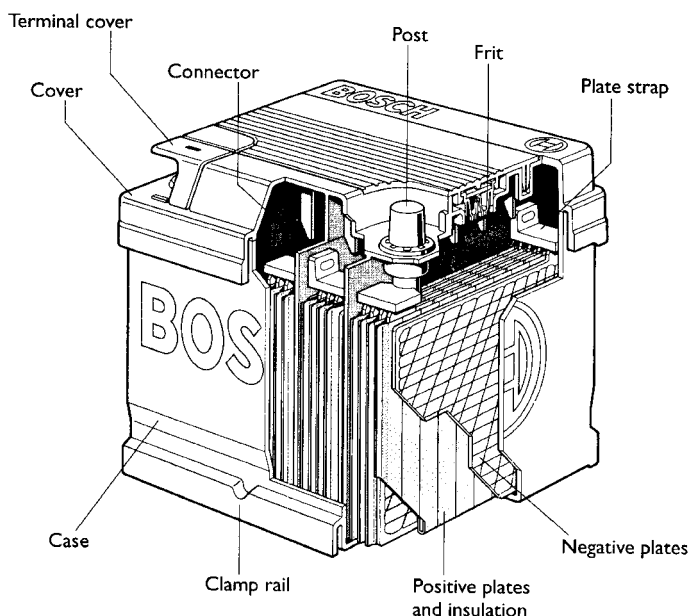- Electrolyte strength.
- Current demanded.

Figure 3.2 Lead-acid battery

The actual current supplied therefore determines the overall capacity of a battery. The rating of a battery has to specify the current output and the time.

Ampere hour capacity

This is now seldom used but describes how much current the battery is able to supply for either 10 or 20 hours. The 20-hour figure is the most common. For example, a battery quoted as being 44 Ah (ampere-hour) will be able, if fully charged, to supply 2.2 A for 20 hours before being completely discharged (cell voltage above 1.75 V).

Reserve capacity

A system used now on all new batteries is reserve capacity. This is quoted as a time in minutes for which the battery will supply 25 A at 25 °C to a final voltage of 1.75 V per cell. This is used to give an indication of how long the battery could run the car if the charging system was not working. Typically, a 44 Ah battery will have a reserve capacity of about 60 minutes.

Cold cranking amps

Batteries are given a rating to indicate performance at high current output and at low temperature. A typical value of 170 A means that the battery will supply this current for one minute at a temperature of −18 °C, at which point the cell voltage will fall to 1.4 V (BS – British Standards).

Note that the overall output of a battery is much greater when spread over a longer time. As mentioned above, this is because the chemical reaction can only work at a certain speed. Figure 3.3 shows the above three discharge characteristics and how they can be compared.

The cold cranking amps (CCA) capacity rating methods do vary to some extent; British standards, DIN standards and SAE standards are the three main examples.

Standard	Time (seconds)
BS	60
DIN	30
SAE	30

In summary, the capacity of a battery is the amount of electrical energy that can be obtained from it. It is usually given in ampere-hours (Ah), reserve capacity (RC) and cold cranking amps (CCA).

- A 40 Ah battery means it should give 2 A for 20 hours.
- The reserve capacity indicates the time in minutes for which the battery will supply 25 A at 25 °C.

- Cold cranking current indicates the maximum battery current at −18 °C (0 °F) for a set time (standards vary).

A battery for normal light vehicle use may be rated as follows: 44 Ah, 60 RC and 170 A CCA (BS). A 'heavy duty' battery will have the same Ah rating as its 'standard duty' counterpart, but it will have a higher CCA and RC.

Maintenance and charging

Maintenance

By far the majority of batteries now available are classed as 'maintenance free'. This implies that little attention is required during the life of the battery. Earlier batteries and some heavier types do, however, still require the electrolyte level to be checked and topped up periodically. Battery posts are still a little prone to corrosion and hence the usual service of cleaning with hot water if appropriate and the application of petroleum jelly or proprietary terminal grease is still recommended. Ensuring that the battery case and, in particular, the top remains clean, will help to reduce the rate of self-discharge.

The state of charge of a battery is still very important and, in general, it is not advisable to allow the state of charge to fall below 70% for long periods as the sulphate on the plates can harden, making recharging difficult. If a battery is to be stored for a long period (more than a few weeks), then it must be recharged every so often to prevent it from becoming sulphated. Recommendations vary but a recharge every six weeks is a reasonable suggestion.

Charging the lead-acid battery

The recharging recommendations of battery manufacturers vary slightly. The following methods,
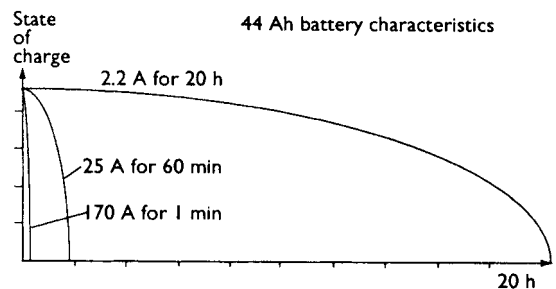

Figure 3.3 Battery discharge characteristics compared

however, are reasonably compatible and should not cause any problems. The recharging process must 'put back' the same ampere-hour capacity as was used on discharge plus a bit more to allow for losses. It is therefore clear that the main question about charging is not how much, but at what rate.

The old recommendation was that the battery should be charged at a tenth of its ampere-hour capacity for about 10 hours or less. This is assuming that the ampere-hour capacity is quoted at the 20 hour rate, as a tenth of this figure will make allowance for the charge factor. This figure is still valid, but as ampere-hour capacity is not always used nowadays, a different method of deciding the rate is necessary. One way is to set a rate at 1/16 of the reserve capacity, again for up to 10 hours. The final suggestion is to set a charge rate at 1/40 of the cold start

performance figure, also for up to 10 hours. Clearly, if a battery is already half charged, half the time is required to recharge to full capacity.

The above suggested charge rates are to be recommended as the best way to prolong battery life. They do all, however, imply a constant current charging source. A constant voltage charging system is often the best way to charge a battery. This implies that the charger, an alternator on a car for example, is held at a constant level and the state of charge in the battery will determine how much current will flow. This is often the fastest way to recharge a flat battery. The two ways of charging are represented in Figure 3.4. This shows the relationship between charging voltage and the charging current. If a constant voltage of less than 14.4 V is used then it is not possible to cause excessive gassing and this method is particularly appropriate for sealed batteries.

Boost charging is a popular technique often applied in many workshops. It is not recommended as the best method but, if correctly administered and not repeated too often, is suitable for most batteries. The key to fast or boost charging is that the battery temperature should not exceed $43\,°C$. With sealed batteries it is particularly important not to let the battery create excessive gas in order to prevent the build-up of pressure. A rate of about five times the 'normal' charge setting will bring the battery to 78–80% of its full capacity within approximately one hour. Table 3.1 summarizes the charging techniques for a lead-acid battery. Figure 3.5 shows a typical battery charger.

Figure 3.4 Two ways of charging a battery showing the relationship between charging voltage and charging current

Diagnosing lead-acid battery faults

Servicing batteries

In use, a battery requires very little attention other than the following when necessary:

● Clean corrosion from terminals using hot water.
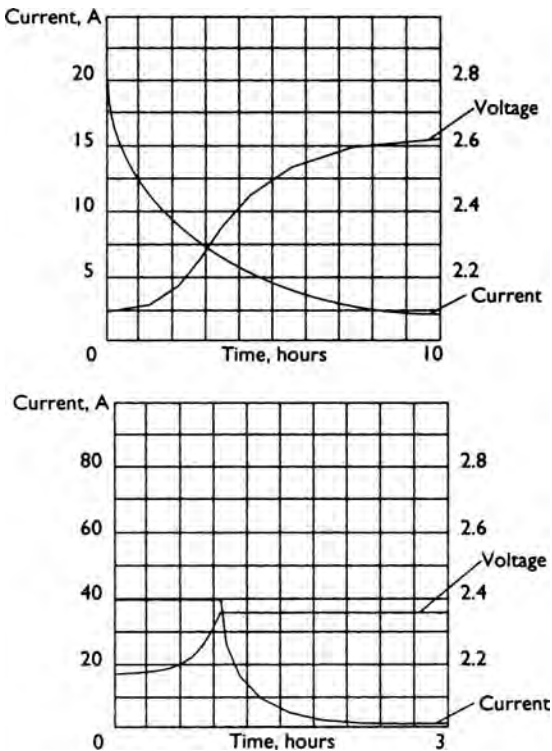● Terminals should be smeared with petroleum jelly or Vaseline, *not* ordinary grease.

Table 3.1 Charging techniques for a lead-acid battery

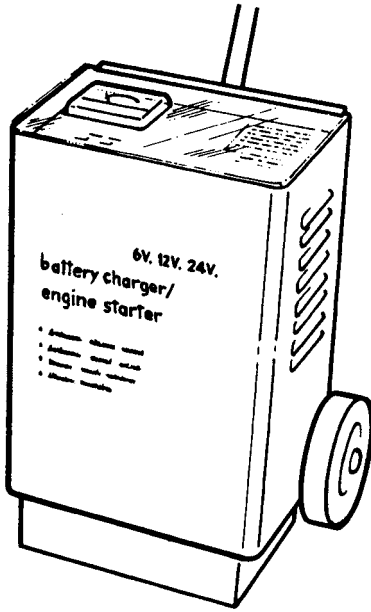| Charging method	Notes
Constant voltage	Will recharge any battery in 7 hours or less without any risk of overcharging (14.4 V maximum).
Constant current	Ideal charge rate can be estimated as: 1/10 of Ah capacity, 1/16 of reserve capacity or 1/40 of cold start current (charge time of 10–12 hours or pro rata original state).
Boost charging	At no more than five times the ideal rate, a battery can be brought up to about 70% of charge in about one hour.

Figure 3.5 Battery charger

Table 3.2 Common problems with lead-acid batteries and their likely causes

Symptom or fault	Likely causes
Low state of charge	Charging system fault
	Unwanted drain on battery
	Electrolyte diluted
	Incorrect battery for application
Low capacity	Low state of charge
	Corroded terminals
	Impurities in the electrolyte
	Sulphated
	Old age – active material fallen from the plates
Excessive gassing and temperature	Overcharging
	Positioned too near exhaust component
Short circuit cell	Damaged plates and insulators
	Build-up of active material in sediment trap
Open circuit cell	Broken connecting strap
	Excessive sulphation
	Very low electrolyte
Service life shorter than expected	Excessive temperature
	Battery has too low a capacity
	Vibration excessive
	Contaminated electrolyte
	Long periods of not being used
	Overcharging

- Battery tops should be clean and dry.
- If not sealed, cells should be topped up with distilled water 3 mm above the plates.
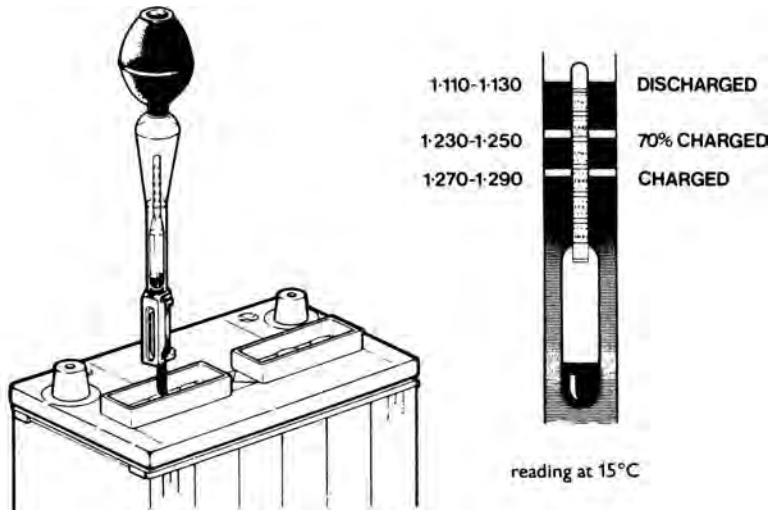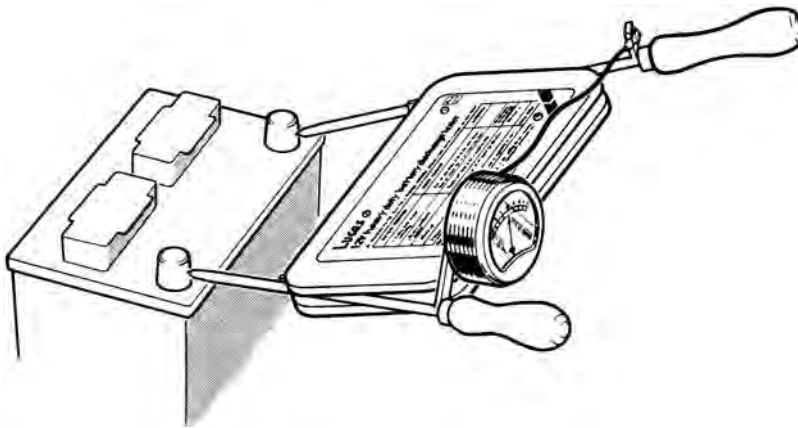- The battery should be securely clamped in position.

Battery faults

Any electrical device can suffer from two main faults; these are either open circuit or short circuit. A battery is no exception but can also suffer from other problems, such as low charge or low capacity. Often a problem – apparently with the vehicle battery – can be traced to another part of the vehicle such as the charging system. Table 3.2 lists all of the common problems encountered with lead-acid batteries, together with typical causes.

Repairing modern batteries is not possible. Most of the problems listed will require the battery to be replaced. In the case of sulphation it is sometimes possible to bring the battery back to life with a very long low current charge. A fortieth of the ampere-hour capacity or about a 1/200 of the cold start performance, for about 50 hours, is an appropriate rate.

Testing batteries

For testing the state of charge of a non-sealed type of battery, a hydrometer can be used, as shown in Figure 3.6. The hydrometer comprises a syringe that draws electrolyte from a cell, and a float that will float at a particular depth in the electrolyte according to its density. The density or specific gravity is then read from the graduated scale on the float. A fully charged cell should show 1.280, 1.200 when half charged and 1.130 if discharged.

Most vehicles are now fitted with maintenance-free batteries and a hydrometer cannot be used to find the state of charge. This can only be determined from the voltage of the battery, as given in Table 5.3. An accurate voltmeter is required for this test.

A heavy-duty (HD) discharge tester as shown in Figure 5.7 is an instrument consisting of a low-value resistor and a voltmeter connected to a pair of heavy test prods. The test prods are firmly pressed on to the battery terminals. The voltmeter reads the voltage of the battery on heavy discharge of 200–300 A.

Assuming a battery to be in a fully charged condition, a serviceable battery should read about 10 V for a period of about 10 s. A sharply falling battery voltage to below 3 V indicates an unserviceable cell. Note also if any cells are gassing, as this indicates a short circuit. A zero or extremely low reading can indicate an open circuit cell. When using the HD tester, the following precautions must be observed:

- Blow gently across the top of the battery to remove flammable gases.
- The test prods must be positively and firmly pressed into the lead terminals of the battery to minimize sparking.
- It should not be used while a battery is on charge.

Figure 3.6 Hydrometer test of a battery

Figure 3.7 Heavy duty discharge test

Table 3.3 State of charge of a battery

Battery volts at 20°C	State of charge
12.0	Discharged (20% or less)
12.3	Half charged (50%)
12.7	Charged (100%)

Safety

The following points must be observed when working with batteries:

- Good ventilation.
- Protective clothing.
- Supply of water available (running water preferable).
- First aid equipment available, including eye-wash.
- No smoking or naked lights permitted.

Advanced battery technology

Electrochemistry

Electrochemistry is a very complex and wide-ranging science. This section is intended only to scratch the surface by introducing important terms and concepts. These will be helpful with the understanding of vehicle battery operation.

The branch of electrochemistry of interest here is the study of galvanic cells and electrolysis. When an electric current is passed through an electrolyte it causes certain chemical reactions and a migration of material. Some chemical reactions, when carried out under certain conditions will produce electrical energy at the expense of the free energy in the system.

The reactions of most interest are those that are reversible, in other words they can convert electrical

energy into chemical energy and vice versa. Some of the terms associated with electrochemistry can be confusing. The following is a selection of terms and names with a brief explanation of each.

Anion: The negative charged ion that travels to the positive terminal during electrolysis.

Anode: Positive electrode of a cell.

Catalyst: A substance that significantly increases the speed of a chemical reaction without appearing to take part in it.

Cation: The positively charged ion that travels to the negative terminal during electrolysis.

Cathode: The negative electrode of a cell.

Diffusion: The self-induced mixing of liquids or gases.

Dissociation: The molecules or atoms in a solution decomposing into positive and negative ions. For example, sulphuric acid (H_2SO_4) dissociates into H^{++}, H^{++} (two positive ions or cations, which are attracted to the cathode), and SO_4^{--} (negative ions or anions, which are attracted to the anode).

Electrode: Plates of a battery or an electrolysis bath suspended in the electrolyte.

Electrolysis: Conduction of electricity between two electrodes immersed in a solution containing ions (electrolyte), which causes chemical changes at the electrodes.

Electrolyte: An ion-conducting liquid covering both electrodes.

Ion: A positively or negatively charged atomic or molecular particle.

Secondary galvanic cell: A cell containing electrodes and an electrolyte, which will convert electrical energy into chemical energy when being charged, and the reverse during discharge.

Electrolytic conduction

Electricity flows through conductors in one of two ways. The first is by electron movement, as is the case with most metals. The other type of flow is by ionic movement, which may be charged atoms or molecules. For electricity to flow through an electrolyte, ion flow is required.

To explain electrolytic conduction, which is current flow through a liquid, sulphuric acid (H_2SO_4) is the best electrolyte example to choose. When in an aqueous solution (mixed with water), sulphuric acid dissociates into H^{++}, H^{++} and SO_4^{--}, which are positive and negative ions. The positive charges are attracted to the negative electrode and the negative charges are attracted to the positive electrode. This movement is known as ion flow or ion drift.

Ohm's Law and electrolytic resistance

The resistance of any substance depends on the following variables:

● Nature of the material.
● Temperature.
● Length.
● Cross-sectional area.

This is true for an electrolyte as well as solid conductors. Length and cross-sectional area have straightforward effects on the resistance of a sample, be it a solid or a liquid. Unlike most metals however, which have a positive temperature coefficient, electrolytes are generally the opposite and have a negative temperature coefficient.

The nature of the material or its conductance (the reciprocal of resistance) is again different between solids and liquids. Different substances have different values of resistivity, but with electrolytes the concentration is also important.

Electrochemical action of the lead-acid battery

A fully charged lead-acid battery consists of lead peroxide (PbO_2) as the positive plates, spongy lead (Pb) as the negative plates and diluted sulphuric acid (H_2SO_4) + (H_2O). The dilution of the electrolyte is at a relative density of 1.28. The lead is known as the active material and, in its two forms, has different valencies. This means a different number of electrons exists in the outer shell of the pure lead than when present as a compound with oxygen. The lead peroxide has, in fact, a valency of +iv (four electrons missing).

As discussed earlier in this chapter, when sulphuric acid is in an aqueous solution (mixed with water), it dissociates into charged ions H^{++}, H^{++} and SO_4^{--}. From the 'outside', the polarity of the electrolyte appears to be neutral as these charges cancel out. The splitting of the electrolyte into these parts is the reason that a charging or discharging current can flow through the liquid.

The voltage of a cell is created due to the ions (charged particles) being forced into the solution from the electrodes by the solution pressure. Lead will give up two positively charged atoms, which have given up two electrons, into the liquid. As a result of giving up two positively charged particles, the electrode will now have an excess of electrons and hence will take on a negative polarity with respect to the electrolyte. If a further electrode is immersed into the electrolyte, different potentials

will develop at the two electrodes and therefore a potential difference will exist between the two. A lead-acid battery has a nominal potential difference of 2 V. The electrical pressure now present between the plates results in equilibrium within the electrolyte. This is because the negative charges on one plate exert an attraction on the positive ions that have entered the solution. This attraction has the same magnitude as the solution pressure and hence equilibrium is maintained.

When an external circuit is connected to the cell, the solution pressure and attraction force are disrupted. This allows additional charged particles to be passed into and through the electrolyte. This will only happen, however, if the external voltage pressure is greater than the electrical tension within the cell. In simple terms this is known as the charging voltage.

When a lead-acid cell is undergoing charging or discharging, certain chemical changes take place. These can be considered as two reactions, one at the positive plate and one at the negative plate. The electrode reaction at the positive plate is a combination of equations (a) and (b).

$$\text{(a)} \quad PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{++} + 2H_2O$$
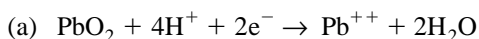
The lead peroxide combines with the dissociated hydrogen and tends to become lead and water.

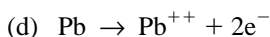$$\text{(b)} \quad Pb^{++} + SO_4^{--} \rightarrow PbSO_4$$

The lead now tends to combine with the sulphate from the electrolyte to become lead sulphate. This gives the overall reaction at the positive pole as:

$$\text{(c)} \quad \text{(a + b)} \quad PbO_2 + 4H^+ + SO_4^{--} + 2e^- \rightarrow \\ PbSO_4 + 2H_2O$$
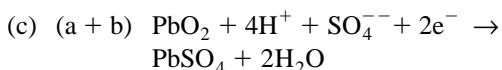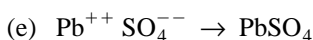
There is a production of water (a) and a deposition of lead sulphate (b) together with a consumption of sulphuric acid.

The electrode reaction at the negative plate is:

$$\text{(d)} \quad Pb \rightarrow Pb^{++} + 2e^-$$

The neutral lead loses two negative electrons to the solution, and becomes positively charged.

$$\text{(e)} \quad Pb^{++} \; SO_4^{--} \rightarrow PbSO_4$$

This then tends to attract the negatively charged sulphate from the solution and the pole becomes lead sulphate. The overall reaction at the negative pole is therefore:

$$\text{(f)} \quad \text{(d + e)} \quad Pb + SO_4^{--} \rightarrow PbSO_4 + 2e^-$$

This reaction leads to a consumption of sulphuric acid and the production of water as the battery is discharged.

The reverse of the above process is when the battery is being charged. The process is the reverse of that described above. The reactions involved in the charging process are listed below.

The charging reaction at the negative electrode:

$$\text{(g)} \quad PbSO_4 + 2e^- + 2H^+ \rightarrow Pb + H_2SO_4$$
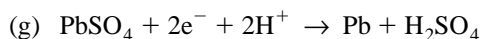
The electrons from the external circuit ($2e^-$) combine with the hydrogen ions in the solution ($2H^+$) and then the sulphate to form sulphuric acid as the plate tends to become lead. The reaction at the positive pole is:

$$\text{(h)} \quad PbSO_4 - 2e^- + 2H_2O \rightarrow PbO_2 \\ + H_2SO_4 + 2H^+$$
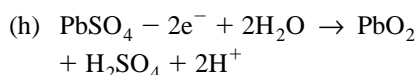
The electrons given off to the external circuit ($2e^-$), release hydrogen ions into the solution ($2H^+$). This allows the positive plate to tend towards lead peroxide, and the concentration of sulphuric acid in the electrolyte to increase.

The net two-way chemical reaction is the sum of the above electrode processes:

$$\text{(i)} \quad \text{(c + f or g + h)} \\ PbO_2 + 2H_2SO_4 + Pb \leftrightarrow 2PbSO_4 \\ + 2H_2O$$
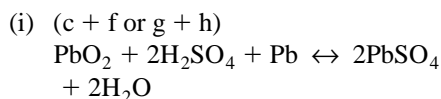
This two-way or reversible chemical reaction (charged on the left and discharged on the right), describes the full process of the charge and discharge cycle of the lead-acid cell.

The other reaction of interest in a battery is that of gassing after it has reached the fully charged condition. This occurs because once the plates of the battery have become 'pure' lead and lead peroxide, the external electrical supply will cause the water in the electrolyte to decompose. This gassing voltage for a lead-acid battery is about 2.4 V. This gassing causes hydrogen and oxygen to be given off resulting in loss of water (H_2O), and an equally undesirable increase in electrolyte acid density.

The reaction, as before, can be considered for each pole of the battery in turn.
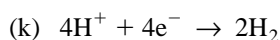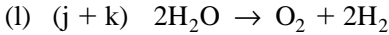
At the positive plate:

$$\text{(j)} \quad 2H_2O - 4e^- \rightarrow O_2 + 4H^+$$

At the negative plate:

$$\text{(k)} \quad 4H^+ + 4e^- \rightarrow 2H_2$$
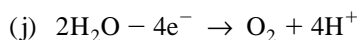
Table 3.4 Factors affecting the voltage of a battery

Acid density	Cell voltage	Battery voltage	% charge
1.28	2.12	12.7	100
1.24	2.08	12.5	70
1.20	2.04	12.3	50
1.15	1.99	12.0	20
1.12	1.96	11.8	0

The sum of these two equations gives the overall result of the reaction;

$$(l) \quad (j + k) \quad 2H_2O \rightarrow O_2 + 2H_2$$

It is acceptable for gassing to occur for a short time to ensure all the lead sulphate has been converted to either lead or lead peroxide. It is the material of the grids inside a battery that contribute to the gassing. With sealed batteries this is a greater problem but has been overcome to a large extent by using lead-calcium for the grid material in place of the more traditional lead-antimony.

The voltage of a cell and hence the whole battery is largely determined by the concentration of the acid in the electrolyte. The temperature also has a marked effect. This figure can be calculated from the mean electrical tension of the plates and the concentration of ions in solution. Table 3.4 lists the results of these calculations at $27\,^\circ$C. As a rule of thumb, the cell voltage is about 0.84 plus the value of the relative density.

It is accepted that the terminal voltage of a lead-acid cell must not be allowed to fall below 1.8 V as, apart from the electrolyte tending to become very close to pure water, the lead sulphate crystals grow markedly making it very difficult to recharge the battery.

Characteristics

The following headings are the characteristics of a battery that determine its operation and condition.

Internal resistance

Any source of electrical energy can be represented by the diagram shown in Figure 3.8. This shows a perfect voltage source in series with a resistor. This is used to represent the reason why the terminal voltage of a battery drops when a load is placed across it. As an open circuit, no current flows through the internal resistance and hence no voltage is dropped. When a current is drawn from the source a voltage drop across the internal resistance will occur. The actual value can be calculated as follows.
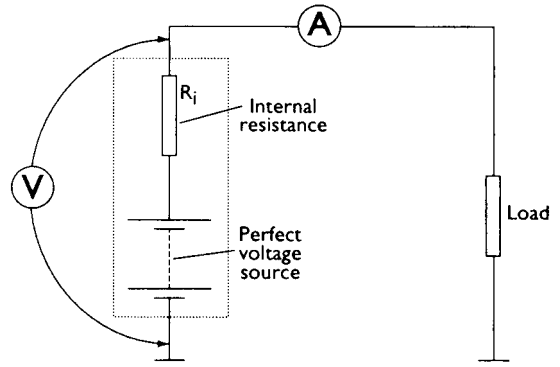

Figure 3.8 Equivalent circuit of an electrical supply showing a perfect voltage source in series with a resistor

Connect a voltmeter across the battery and note the open circuit voltage, for example 12.7 V. Connect an external load to the battery, and measure the current, say 50 A. Note again the on-load terminal voltage of the battery, for example 12.2 V.

A calculation will determine the internal resistance:

$$R_i = (U - V)/I$$

where U = open circuit voltage, V = on-load voltage, I = current, R_i = internal resistance.

For this example the result of the calculation is $0.01\,\Omega$.

Temperature and state of charge affect the internal resistance of a battery. The internal resistance can also be used as an indicator of battery condition – the lower the figure, the better the condition.

Efficiency

The efficiency of a battery can be calculated in two ways, either as the ampere-hour efficiency or the power efficiency.

$$\text{Ah efficiency} = \frac{\text{Ah discharging}}{\text{Ah charging}} \times 100\%$$

At the 20 hour rate this can be as much as 90%. This is often quoted as the reciprocal of the efficiency figure; in this example about 1.1, which is known as the charge factor.

$$\text{Energy efficiency} = \frac{P_d \times t_d}{P_c \times t_c} \times 100\%$$

where P_d = discharge power, t_d = discharge time, P_c = charging power, t_c = charging time.

A typical result of this calculation is about 75%. This figure is lower than the Ah efficiency as it takes into account the higher voltage required to force the charge into the battery.

Self-discharge

All batteries suffer from self-discharge, which means that even without an external circuit the state of charge is reduced. The rate of discharge is of the order of 0.2–1% of the Ah capacity per day. This increases with temperature and the age of the battery. It is caused by two factors. First, the chemical process inside the battery changes due to the material of the grids forming short circuit voltaic couples between the antimony and the active material. Using calcium as the mechanical improver for the lead grids reduces this. Impurities in the electrolyte, in particular trace metals such as iron, can also add to self-discharge.

Second, a leakage current across the top of the battery, particularly if it is in a poor state of cleanliness, also contributes to the self-discharge. The fumes from the acid together with particles of dirt can form a conducting film. This problem is much reduced with sealed batteries.

Developments in electrical storage

Lead-acid battery developments

Lead-acid batteries have not changed much from the very early designs (invented by Gaston Plante in 1859). Incremental changes and, in particular, the development of accurate charging system control has allowed the use of sealed and maintenance-free batteries. Figure 3.9 shows a typical modern battery.

The other main developments have been to design batteries for particular purposes. This is particularly appropriate for uses such as supplementary batteries in a caravan or as power supplies for lawn mowers and other traction uses. These batteries are designed to allow deep discharge and, in the case of caravan batteries, may also have vent tubes fitted to allow gases to be vented outside. Some batteries are designed to withstand severe vibration for use on plant-type vehicles.

The processes in lead-acid batteries are very similar, even with variations in design. However, batteries using a gel in place of liquid electrolyte are worth a mention. These batteries have many advantages in that they do not leak and are more resistant to poor handling.

The one main problem with using a gel electrolyte is that the speed of the chemical reaction is reduced. Whilst this is not a problem for some types of supply, the current required by a vehicle starter is very high for a short duration. The cold cranking
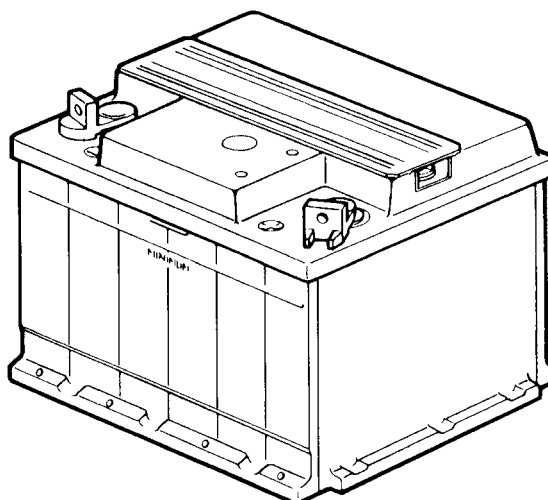

Figure 3.9 Modern vehicle battery

amps (CCA) capacity of this type of battery is therefore often lower than the equivalent-sized conventional battery.

The solid-gel type electrolyte used in some types of these batteries is thixotropic. This means that, due to a high viscosity, the gel will remain immobile even if the battery is inverted. A further advantage of a solid gel electrolyte is that a network of porous paths is formed through the electrolyte. If the battery is overcharged, the oxygen emitted at the positive plate will travel to the negative plate, where it combines with the lead and sulphuric acid to form lead sulphate and water:

$$O_2 + 2Pb = 2PbO$$
$$PbO + H_2SO_4 = PbSO_4 + H_2O$$
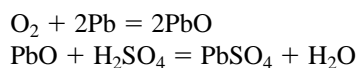
This reforming of the water means the battery is truly maintenance free. The recharging procedure is very similar to the more conventional batteries.

To date, gel-type batteries have not proved successful for normal motor vehicle use, but are an appropriate choice for specialist performance vehicles that are started from an external power source. Ordinary vehicle batteries using a gel electrolyte appeared on the market some years ago accompanied by great claims of reliability and long life. However, these batteries did not become very popular. This could have been because the cranking current output was not high enough due to the speed of the chemical reaction.

An interesting development in 'normal' lead-acid batteries is the use of lead-antimony (PbSb) for the positive plate grids and lead-calcium (PbCa) for the negative plate grids. This results in a significant reduction in water loss and an increase in service

life. The plates are sealed in microporous pocket-type separators, on each side of which are glass-fibre reinforcing mats. The pocket separators collect all the sludge and hence help to keep the electrolyte in good condition.

Alkaline batteries

Lead-acid batteries traditionally required a considerable amount of servicing to keep them in good condition, although this is not now the case with the advent of sealed and maintenance-free batteries. However, when a battery is required to withstand a high rate of charge and discharge on a regular basis, or is left in a state of disuse for long periods, the lead-acid cell is not ideal. Alkaline cells on the other hand require minimum maintenance and are far better able to withstand electrical abuse such as heavy discharge and over-charging.

The disadvantages of alkaline batteries are that they are more bulky, have lower energy efficiency and are more expensive than a lead-acid equivalent. When the lifetime of the battery and servicing requirements are considered, the extra initial cost is worth it for some applications. Bus and coach companies and some large goods-vehicle operators have used alkaline batteries.

Alkaline batteries used for vehicle applications are generally the nickel-cadmium type, as the other main variety (nickel-iron) is less suited to vehicle use. The main components of the nickel-cadmium – or Nicad – cell for vehicle use are as follows:

- positive plate – nickel hydrate (NiOOH);
- negative plate – cadmium (Cd);
- electrolyte – potassium hydroxide (KOH) and water (H_2O).

The process of charging involves the oxygen moving from the negative plate to the positive plate, and the reverse when discharging. When fully charged, the negative plate becomes pure cadmium and the positive plate becomes nickel hydrate. A chemical equation to represent this reaction is given next but note that this is simplifying a more complex reaction.

$$2NiOOH + Cd + 2H_2O + KOH \leftrightarrow$$
$$2Ni(OH)_2 + CdO_2 + KOH$$
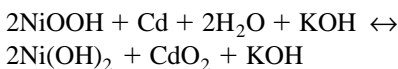
The $2H_2O$ is actually given off as hydrogen (H) and oxygen (O_2) as gassing takes place all the time during charge. It is this use of water by the cells that indicates they are operating, as will have been noted from the equation. The electrolyte does not change during the reaction. This means that a relative density reading will not indicate the state of charge. These batteries do not suffer from over-charging
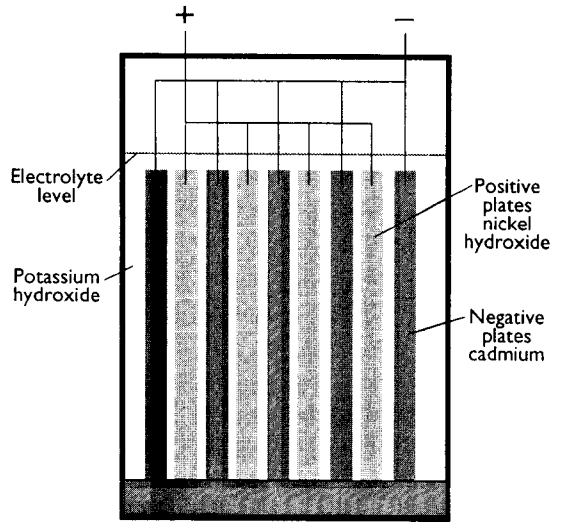

Figure 3.10 Simplified representation of a Nicad alkaline battery cell

because once the cadmium oxide has changed to cadmium, no further reaction can take place.

The cell voltage of a fully charged cell is 1.4 V but this falls rapidly to 1.3 V as soon as discharge starts. The cell is discharged at a cell voltage of 1.1 V. Figure 3.10 shows a simplified representation of a Nicad battery cell.

Ni-MH or nickel-metal-hydride batteries show some promise for electric vehicle use.

The ZEBRA battery

The Zero Emissions Battery Research Activity (ZEBRA) has adopted a sodium-nickel-chloride battery for use in its electric vehicle programme. This battery functions on an electrochemical principle. The base materials are nickel and sodium chloride. When the battery is charged, nickel chloride is produced on one side of a ceramic electrolyte and sodium is produced on the other. Under discharge, the electrodes change back to the base materials. Each cell of the battery has a voltage of 2.58 V.

The battery operates at an internal temperature of 270–350 °C, requiring a heat-insulated enclosure. The whole unit is 'vaccum packed' to ensure that the outer surface never exceeds 30 °C. The ZEBRA battery has an energy density of 90 Wh/kg, which is more than twice that of a lead-acid type.

When in use on the electric vehicle (EV), the battery pack consists of 448 individual cells rated at 289 V. The energy density is 81 Wh/kg; it has a mass of 370 kg (over 1/4 of the total vehicle mass) and measures $993 \times 793 \times 280$ mm^3. The battery pack can be recharged in just one hour using an

external power source. It is currently in use/development on the Mercedes A-class vehicle.

Ultra-capacitors

Ultra-capacitors are very high capacity but (relatively) low size capacitors. This is achieved by employing several distinct electrode materials prepared using special processes. Some state-of-the-art ultra-capacitors are based on high surface area, ruthenium dioxide (RuO_2) and carbon electrodes. Ruthenium is extremely expensive and available only in very limited amounts.

Electrochemical capacitors are used for high-power applications such as cellular electronics, power conditioning, industrial lasers, medical equipment, and power electronics in conventional, electric and hybrid vehicles. In conventional vehicles, ultra-capacitors could be used to reduce the need for large alternators for meeting intermittent high peak power demands related to power steering and braking. Ultra-capacitors recover braking energy dissipated as heat and can be used to reduce losses in electric power steering.

One system in use on a hybrid bus uses 30 ultra-capacitors to store 1600 kJ of electrical energy (20 farads at 400 V). The capacitor bank has a mass of 950 kg. Use of this technology allows recovery of energy, such as when braking, that would otherwise have been lost. The capacitors can be charged in a very short space of time. The energy in the capacitors can also be used very quickly, such as for rapid acceleration.

Fuel cells

The energy of oxidation of conventional fuels, which is usually manifested as heat, may be converted directly into electricity in a fuel cell. All oxidations involve a transfer of electrons between the fuel and oxidant, and this is employed in a fuel cell to convert the energy directly into electricity. All battery cells involve an oxide reduction at the positive pole and an oxidation at the negative during some part of their chemical process. To achieve the separation of these reactions in a fuel cell, an anode, a cathode and electrolyte are required. The electrolyte is fed directly with the fuel.

It has been found that a fuel of hydrogen when combined with oxygen proves to be a most efficient design. Fuel cells are very reliable and silent in operation, but at present are very expensive to construct. Figure 3.11 shows a simplified representation of a fuel cell.
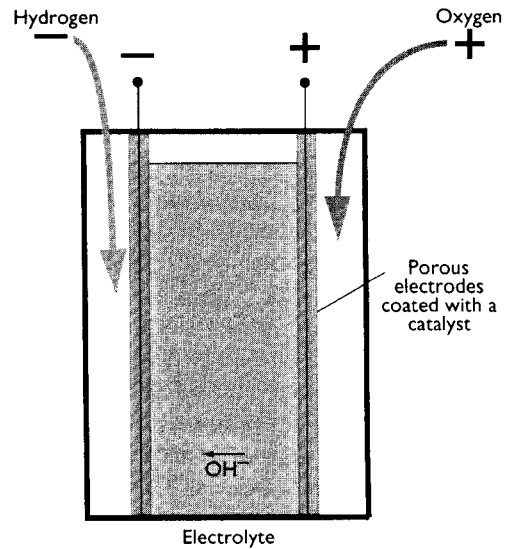

Figure 3.11 Representation of a fuel cell

Operation of one type of fuel cell is such that as hydrogen is passed over an electrode (the anode) of porous nickel, which is coated with a catalyst, the hydrogen diffuses into the electrolyte. This causes electrons to be stripped off the hydrogen atoms. These electrons then pass through the external circuit. Negatively charged hydrogen anions (OH^-) are formed at the electrode over which oxygen is passed such that it also diffuses into the solution. These anions move through the electrolyte to the anode. The electrolyte, which is used, is a solution of potassium hydroxide (KOH). Water is formed as the by-product of a reaction involving the hydrogen ions, electrons and oxygen atoms. If the heat generated by the fuel cell is used, an efficiency of over 80% is possible, together with a very good energy density figure. A single fuel cell unit is often referred to as a 'stack'.

The working temperature of these cells varies but about 200 °C is typical. High pressure is also used and this can be of the order of 30 bar. It is the pressures and storage of hydrogen that are the main problems to be overcome before the fuel cell will be a realistic alternative to other forms of storage for the mass market. The next section, however, explains one way around the 'hydrogen' problem.

Fuel cells in use on 'urban transport' vehicles typically use 20×10 kW stacks (200 kW) operating at 650 V.

Fuel cell developments

Some vehicle manufacturers have moved fuel cell technology nearer to production reality with an on-board system for generating hydrogen from

Figure 3.12 Mercedes-Benz A-class

Figure 3.13 NECAR – Fuel cells in a Mercedes A-class

methanol. Daimler-Benz, now working with the Canadian company Ballard Power Systems, claimed the system as a 'world first'. The research vehicle is called NECAR (New Electric Car). It is based on the Mercedes-Benz's 'A-class' model (Figure 3.12).

In the system, a reformer converts the methanol into hydrogen by water vapour reformation. The hydrogen gas is then supplied to fuel cells to react with atmospheric oxygen, which in turn produces electric energy.

The great attraction of methanol is that it can easily fit into the existing gasoline/diesel infrastructure of filling stations and does not need highly specialized equipment or handling. It is easy to store on-board the vehicle, unlike hydrogen which needs heavy and costly tanks. At the time of writing the NECAR (Figure 3.13) has a range of about 400 km on a 40 litre methanol tank. Consideration is also being given to multifuel hydrogen sourcing.

The methanol reformer technology used has benefited from developments that have allowed the system to become smaller and more efficient compared with earlier efforts. The result is a 470 mm high unit located in the rear of the A-class, in which the reformer directly injects hydrogen into the fuel cells. Hydrogen production occurs at a temperature of some $280\,°C$. Methanol and water vaporize to yield hydrogen (H), carbon dioxide (CO_2), and carbon monoxide (CO). After catalytic oxidation of the CO, the hydrogen gas is fed to the negative pole of the fuel cell where a special plastic foil, coated with a platinum catalyst and sandwiched between two electrodes, is located. The conversion of the hydrogen into positively charged protons and negatively charged electrons begins with the arrival of oxygen at the positive pole. The foil is only permeable to protons; therefore, a voltage builds up across the fuel cell.

Sodium sulphur battery

Much research is underway to improve on current battery technology in order to provide a greater energy density for electric vehicles. (Electric traction will be discussed further in a later chapter.) A potential major step forwards however is the sodium sulphur battery, which has now reached production stage. Table 3.5 compares the potential energy density of several types of battery. Wh/kg means watt hours per kilogram or the power it will supply, for how long per kilogram.

Sodium-sulphur batteries have recently reached the production stage and, in common with the other types listed, have much potential; however, all types have specific drawbacks. For example, storing and carrying hydrogen is one problem of fuel cells.

Table 3.5 The potential energy density of several battery types

Battery type	Cell voltage	Energy density (Wh/kg)
Lead-acid	2	30
Nickel-iron/cadmium	1.22	45
Nickel-metal-hydride	1.2	50–80
Sodium-sulphur	2–2.5	90–100
Sodium-nickel-chloride	2.58	90–100
Lithium	3.5	100
H_2/O_2 Fuel cell	~30	500

The sodium-sulphur or NaS battery consists of a cathode of liquid sodium into which is placed a current collector. This is a solid electrode of β-alumina. A metal can that is in contact with the anode (a sulphur electrode) surrounds the whole assembly. The major problem with this system is that the running temperature needs to be 300–350 °C. A heater rated at a few hundred watts forms part of the charging circuit. This maintains the battery temperature when the vehicle is not running. Battery temperature is maintained when in use due to $I^2 R$ losses in the battery.

Each cell of this battery is very small, using only about 15 g of sodium. This is a safety feature because, if the cell is damaged, the sulphur on the outside will cause the potentially dangerous sodium to be converted into polysulphides – which are comparatively harmless. Small cells also have the advantage that they can be distributed around the car. The capacity of each cell is about 10 Ah. These cells fail in an open circuit condition and hence this must be taken into account, as the whole string of cells used to create the required voltage would be rendered inoperative. The output voltage of each cell is about 2 V. Figure 3.14 shows a representation of a sodium-sulphur battery cell.

A problem still to be overcome is the casing material, which is prone to fail due to the very corrosive nature of the sodium. At present, an expensive chromized coating is used.

This type of battery, supplying an electric motor, is becoming a competitor to the internal combustion engine. The whole service and charging infrastructure needs to develop but looks promising. It is estimated that the cost of running an electric vehicle will be as little as 15% of the petrol version, which leaves room to absorb the extra cost of production.

5.6.8 The Swing battery

Some potential developments in battery technology are major steps in the right direction but many new methods involve high temperatures. One major aim
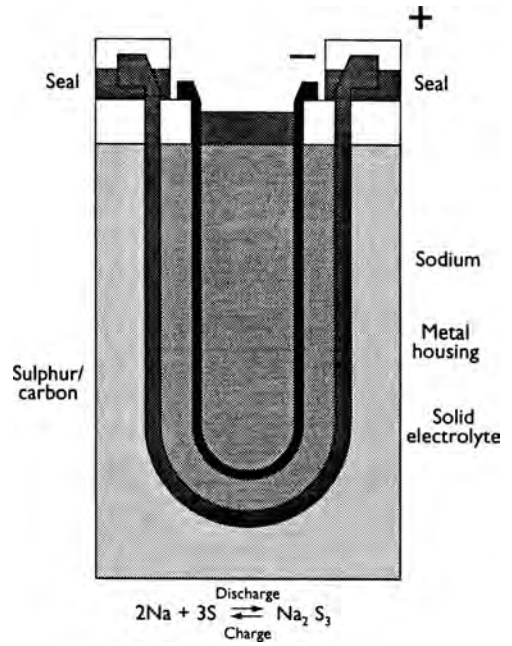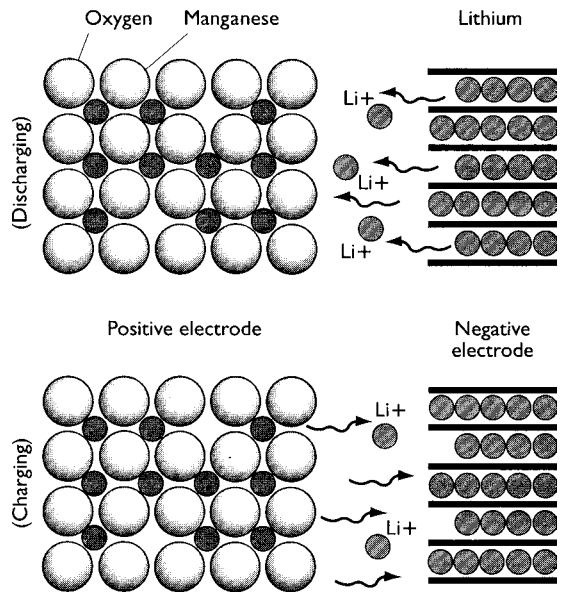

Figure 3.14 Sodium sulphur battery

Figure 3.15 Chemical process of the 'Swing' battery (3.5 V/cell at room temperature)

of battery research is to develop a high performance battery, that works at a normal operating temperature. One new idea is called the 'Swing battery'. Figure 3.15 shows the chemical process of this battery.

The Swing concept batteries use lithium ions. These batteries have a carbon anode and a cathode made of transition metal oxides. Lithium ions are in constant movement between these very thin electrodes in a non-aqueous electrolyte. The next step

planned by the company is to use a solid polymer electrolyte, based on polyethylene oxide instead of the liquid electrolyte.

The Swing process takes place at normal temperatures and gives a very high average cell voltage of 3.5 V, compared with cell voltages of approximately 1.2 V for nickel-cadmium and about 2.1 V for lead-acid or sodium-sulphur batteries. Tests simulating conditions in electric vehicles have demonstrated specific energies of about 100 Wh/kg and 200 Wh/l.

The complexity of the electrical storage system increases with higher operating temperatures, an increased number of cells and with the presence of agitated or recycled electrolytes. To ensure reliable and safe operation, higher and higher demands will be made on the battery management system. This will clearly introduce more cost to the vehicle system as a whole. Consideration must be given not only to specific energy storage but also to system complexity and safety. Figure 3.16 is a comparison of batteries considering energy density and safety factors.

The high temperature systems have, however, proved their viability for use in vehicles. They have already passed a series of abuse tests and other systems are in preparation. A sodium-sulphur battery when fully charged, which is rated at 20 kWh, contains about 10 kg of liquid sodium. Given 100 000 vehicles, 1000 tonnes of liquid sodium will be in use. These quantities have to be encapsulated in two hermetically sealed containers. The Swing concept is still new but offers a potentially safe system for use in the future.
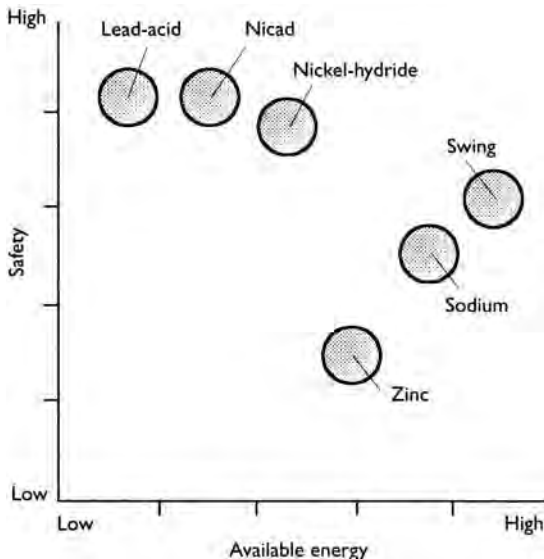

Figure 3.16 Comparison of battery technologies

New developments in batteries

Bosch silver battery – case study

Bosch has launched a new range of batteries for commercial vehicles with innovative silver technology for extreme conditions of use. The new 'Tecmaxx' heavy vehicle battery features exceptionally high reserves of power at very high or low temperatures. In addition, the use of silver-plating means that the Tecmaxx is completely maintenance-free.

The innovative safety design of the new truck battery means that it can even be placed internally in the vehicle body. The newly designed top with Security$^+$ stoppers means that no acid can escape even if the vehicle is subjected to extreme vibration or shaking. The battery can even be tipped on its side by up to 90° without danger. A safety feature incorporated into the top of the battery prevents battery gas from being ignited by sparks or flames.

Figure 3.17 Light vehicle battery showing the charge indicator (Source: Bosch Press)

Figure 3.18 Bosch commercial vehicle battery (Source: Bosch Press)

Any gases forming within the battery – resulting from overloading or overcharging, for example – are removed via the main extractor system. The charge level of the battery can be seen at a glance from its Power Control System charge indicator (Figure 3.17).

The silver-plating and the optimized cold start properties mean that the two Tecmaxx models can be used to replace a range of batteries of varying capacities. The Tecmaxx batteries are available with ratings of 140 and 170 amps/hour (Figure 3.18).

It is interesting to note that two thirds of all assistance to cars provided in winter time are caused by start-up problems – frequently due to weak batteries!

Self-assessment

Questions

1. Describe what a 'lead-acid' battery means.
2. State the three ways in which a battery is generally rated.
3. Make a clearly labelled sketch to show how a 12 V battery is constructed.
4. Explain why a battery is rated or described in different ways.
5. List six considerations when deciding where a vehicle battery should be positioned.
6. Describe how to measure the internal resistance of a battery.
7. Make a table showing three ways of testing the state of charge of a lead-acid battery together with the results.
8. Describe the two methods of recharging a battery.
9. State how the ideal charge rate for a lead-acid battery can be determined.
10. Explain why the 'energy density' of a battery is important.

Assignment

Carry out research into the history of the vehicle battery and makes notes of significant events. Read further about 'new' types of battery and suggest some of their advantages and disadvantages. What are the main limiting factors to battery improvements? Why is the infrastructure for battery 'service and repair' important for the adoption of new technologies?

Multiple choice questions

A 12 volt lead-acid battery has:
1. cells connected in parallel, plates connected in series
2. cells connected in series, plates connected in parallel
3. cells connected in series, plates connected in series
4. cells connected in parallel, plates connected in parallel

The gases given off by a lead-acid battery nearing the end of its charge are:
1. oxygen and nitrogen
2. oxygen and hydrogen
3. helium and hydrogen
4. nitrogen and hydrogen

A lead-acid battery should be topped up with:
1. sulphuric acid
2. distilled water
3. sulphuric acid and distilled water
4. electrolyte at the correct relative density

The electrolyte for a fully charged lead-acid battery has a relative density of approximately:
1. 1.000
2. 1.100
3. 1.280
4. 1.500

The duration of a high rate discharge test should not exceed about:
1. 10 seconds
2. 30 seconds
3. 50 seconds
4. 70 seconds

When a battery is disconnected, the earth lead should always be disconnected first because:
1. the circuit would still be a closed circuit
2. the mechanic could receive a shock
3. it reduces the chance of a short circuit
4. the battery will discharge quicker

Connecting and disconnecting the battery leads with electrical systems switched on may cause:
1. a reduced risk of arcing
2. damage to electronic components
3. discharging the battery
4. low resistance connections

When using a high rate discharge test on a 40 amp/hour capacity battery the current should be set to about:
1. 1 amp
2. 4 amps
3. 40 amps
4. 120 amps

An ideal charge rate for a battery is:
1. 1/10th of the reserve capacity
2. 1/10th of the amp/hour capacity
3. 1/40th of the reserve capacity
4. 1/40th of the charger capacity

When discussing the reasons why a change from 12 V to 42 V batteries is likely in the future, Technician A says this will produce an increase in power for an increased range of accessories. Technician B says this will provide an increase in power but also an increase in maintenance. Who is right?
1. A only
2. B only
3. Both A and B
4. Neither A nor B

Nickel cadmium batteries

The nickel–cadmium battery (NiCd battery or NiCad battery) is a type of rechargeable battery which is developed using nickel oxide hydroxide and metallic cadmium as electrodes.

Ni-Cd batteries excel at maintaining voltage and holding charge when not in use. However, NI-Cd batteries worry about "memory" effect when a partially charged battery is recharged, lowering the future capacity of the battery.
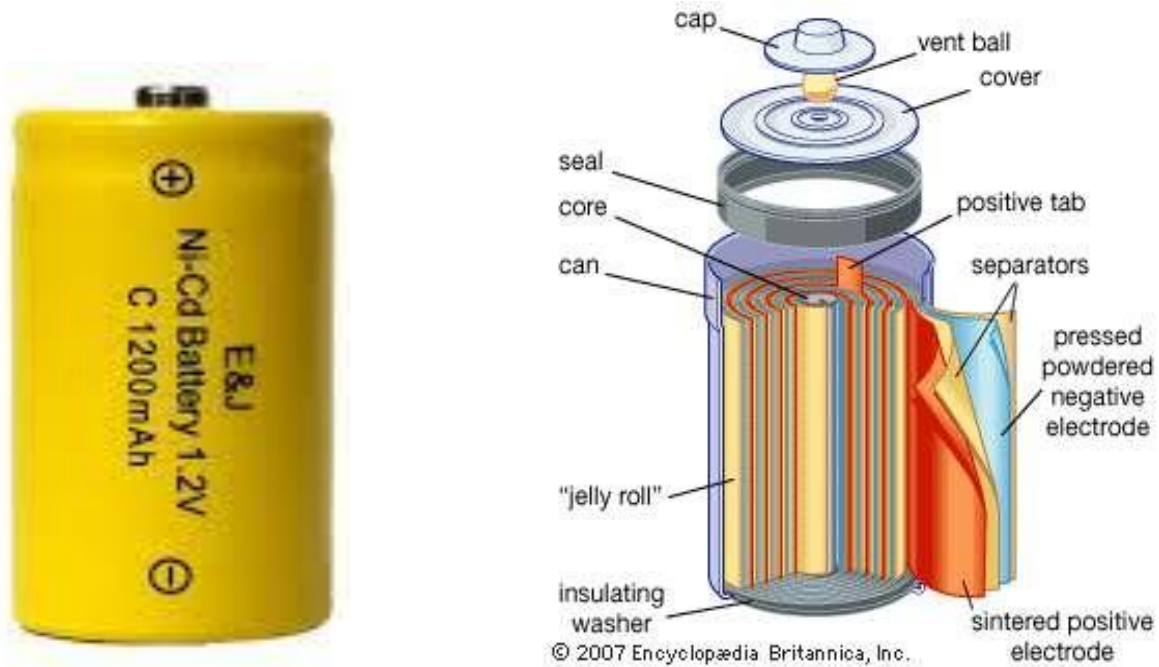
Electrochemistry

A fully charged Ni-Cd cell contains:

- a nickel(III) oxide-hydroxide positive electrode plate
- a cadmium negative electrode plate
- a separator, and
- an alkaline electrolyte (potassium hydroxide).

Ni-Cd batteries usually have a metal case with a sealing plate equipped with a self-sealing safety valve.

The positive and negative electrode plates, isolated from each other by the separator, are rolled in a spiral shape inside the case. This is known as the jelly-roll design and allows a Ni–Cd cell to deliver a much higher maximum current than an equivalent size alkaline cell

- The chemical reactions in a NiCad battery during discharge are:

- At the cadmium electrode:
$$Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$$
- At the nickel electrode:
$$2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$$
- The overall equation is
$$2NiO(OH) + Cd + 2H_2O \rightarrow 2Ni(OH)_2 + Cd(OH)_2.$$

During recharge, the reactions go from right to left. The alkaline electrolyte (commonly KOH) is not consumed in this reaction and therefore its specific gravity, unlike in lead–acid batteries, is not a guide to its state of charge.

Some of the properties of Nickel-Cadmium batteries are listed below.

- Specific Energy: 40-60W-h/kg
- Energy Density: 50-150 W-h/L
- Specific Power: 150W/kg
- Charge/discharge efficiency: 70-90%
- Self-discharge rate: 10%/month
- Cycle durability/life: 2000cycles

History

➢ The first Ni–Cd battery was created by waldemar Jungner of Sweden in 1899.

➢ Thomas Edison patented a nickel– or cobalt–cadmium battery in 1902, and adapted the battery design when he introduced the nickel–iron battery to the US two years after Jungner had built one.

➢ In 1906, Jungner established a factory close to Oskarshamn, Sweden to produce flooded design Ni–Cd batteries.

➢ In 1932 active materials were deposited inside a porous nickel-plated electrode and fifteen years later began on a sealed nickel-cadmium battery.

➢ The first production in the United States began in 1946. Up to this point, the batteries were "pocket type," constructed of nickel-plated steel pockets containing nickel and cadmium active materials.

➢ Since the 2000s, all consumer Ni–Cd batteries use the "Swiss roll" or "jelly-roll" configuration. This design incorporates several layers of positive and negative material rolled into a cylindrical shape. This design reduces internal resistance as there is a greater amount of electrode in contact with the active material in each cell Characteristics

➢ The maximum discharge rate for a Ni–Cd battery varies by size. For a common AA-size cell, the maximum discharge rate is approximately 1.8 amperes; for a D size battery the discharge rate can be as high as 3.5 amperes

➢ Model-aircraft or -boat builders often take much larger currents of up to a hundred amps or so from specially constructed Ni–Cd batteries, which are used to drive main motors.

Properties:

Voltage

Ni–Cd cells have a nominal cell potential of 1.2 volts (V). This is lower than the 1.5 V of alkaline and zinc–carbon primary cells.

Many electronic devices are designed to work with primary cells that may discharge to as low as 0.90 to 1.0 V per cell, the relatively steady 1.2 V of a Ni–Cd cell is enough to allow operation.

Some would consider the near-constant voltage a drawback as it makes it difficult to detect when the battery charge is low.

Ni–Cd batteries used to replace 9 V batteries usually only have six cells, for a terminal voltage of 7.2 volts. While most pocket radios will operate satisfactorily at this voltage.

Charging

Ni–Cd batteries can be charged at several different rates, depending on how the cell was manufactured. The charge rate is measured based on the percentage of the amp-hour capacity the battery is fed as a steady current over the duration of the charge.

The safe temperature range when in use is between −20 °C and 45 °C. During charging, the battery temperature typically stays low, around the same as the ambient temperature (the charging reaction absorbs energy), but as the battery nears full charge the temperature will rise to 45–50 °C. Some battery chargers detect this temperature increase to cut off charging and prevent over-charging.

Ni–Cd battery will self-discharge approximately 10% per month at 20 °C, ranging up to 20% per month at higher temperatures. It is possible to perform a trickle charge at current levels just high enough to offset this discharge rate; to keep a battery fully charged

Overcharging

Sealed Ni–Cd cells consist of a pressure vessel that is supposed to contain any generation of oxygen and hydrogen gases until they can recombine back to water. Such generation typically occurs during rapid charge and discharge, and exceedingly at overcharge condition. If the pressure exceeds the limit of the safety valve, water in the form of gas is lost. Since the vessel is designed to contain an exact amount of electrolyte this loss will rapidly affect the capacity of the cell and its ability to receive and deliver current. To detect all conditions of overcharge demands great sophistication from the charging circuit and a cheap charger will eventually damage even the best quality cells.

➢ **Vented cell batteries**

View of a vented cell aircraft battery from the side
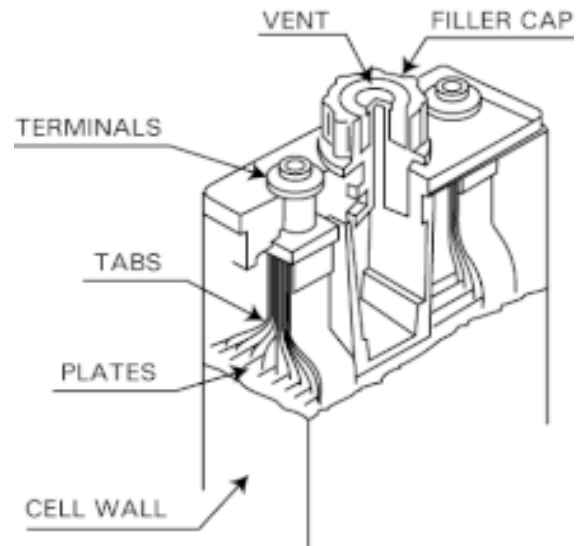
Structure of a cell in a vented cell battery

Vented cell (*wet cell*, *flooded cell*) NiCd batteries are used when large capacities and high discharge rates are required.

Traditional NiCd batteries are of the sealed type, which means that charge gas is normally recombined and they release no gas unless severely overcharged or a fault develops. Unlike typical NiCd cells, which are sealed, vented cells have a vent or low pressure release valve that releases any generated oxygen and hydrogen gases when overcharged or discharged rapidly.

Since the battery is not a pressure vessel, it is safer, weighs less, and has a simpler and more economical structure.

This also means the battery is not normally damaged by excessive rates of overcharge, discharge or even negative charge.

A steel battery box contains the cells connected in series to gain the desired voltage (1.2 V per cell nominal). Cells are usually made of a light and durable polyamide (nylon), with multiple nickel-cadmium plates welded together for each electrode inside.

A separator or liner made of silicone rubber acts as an insulator and a gas barrier between the electrodes.

Cells are flooded with an electrolyte of 30% aqueous solution of potassium hydroxide (KOH).

The specific gravity of the electrolyte does not indicate if the battery is discharged or fully charged but changes mainly with evaporation of water.

The top of the cell contains a space for excess electrolyte and a pressure release vent. Large nickel-plated copper studs and thick interconnecting links assure minimum equivalent series resistance for the battery.

Application

- ➢ used in photographic equipment, hand-held lamps (flashlight or torch), computer-memory standby
- ➢ used in cordless and wireless telephones, emergency lighting
- ➢ Other applications.

Remote-controlled electric model airplanes, boats, and cars, as well as cordless power tools and camera flash units

Eight NiCd batteries in a battery pack

Comparison with other batteries

Recently, nickel–metal hydride and lithium-ion batteries have become commercially available and cheaper, the former type now rivaling Ni–Cd batteries in cost. Where energy density is important, Ni–Cd batteries are now at a disadvantage compared with nickel–metal hydride and lithium-ion batteries. However, the Ni–Cd battery is still very useful in applications requiring very high discharge rates because it can endure such discharge with no damage or loss of capacity.

When compared to other forms of rechargeable battery, the Ni–Cd battery has a number of distinct advantages:

- The batteries are more difficult to damage than other batteries, tolerating deep discharge for long periods. In fact, Ni–Cd batteries in long-term storage are typically stored fully discharged. This is in contrast, for example, to lithium ion batteries, which are less stable and will be permanently damaged if discharged below a minimum voltage.
- The battery performs very well under rough conditions, perfect for use in the portable tools.

- Ni–Cd batteries typically last longer, in terms of number of charge/discharge cycles, than other rechargeable batteries such as lead/acid batteries.
- Compared to lead–acid batteries, Ni–Cd batteries have a much higher energy density. A Ni–Cd battery is smaller and lighter than a comparable lead–acid battery, but not a comparable NiMH or Li-ion battery. In cases where size and weight are important considerations (for example, aircraft), Ni–Cd batteries are preferred over the cheaper lead–acid batteries.
- In consumer applications, Ni–Cd batteries compete directly with alkaline batteries. A Ni–Cd cell has a lower capacity than that of an equivalent alkaline cell, and costs more. However, since the alkaline battery's chemical reaction is not reversible, a reusable Ni–Cd battery has a significantly longer total lifetime. There have been attempts to create rechargeable alkaline batteries, or specialized battery chargers for charging single-use alkaline batteries, but none that has seen wide usage.
- The terminal voltage of a Ni–Cd battery declines more slowly as it is discharged, compared with carbon–zinc batteries. Since an alkaline battery's voltage drops significantly as the charge drops, most consumer applications are well equipped to deal with the slightly lower Ni–Cd cell voltage with no noticeable loss of performance.
- The capacity of a Ni–Cd battery is not significantly affected by very high discharge currents. Even with discharge rates as high as 50C, a Ni–Cd battery will provide very nearly its rated capacity. By contrast, a lead acid battery will only provide approximately half its rated capacity when discharged at a relatively modest 1.5C.
- The maximum continuous current drain of NiCd battery is commonly around 15C. Compared to NiMH battery where usable maximum continuous current drain is not more than 5C.
- Nickel–metal hydride (NiMH) batteries are the newest, and most similar, competitor to Ni–Cd batteries. Compared to Ni–Cd batteries, NiMH batteries have a higher capacity and are less toxic, and are now more cost effective. However, a Ni–Cd battery has a lower self-discharge rate (for example, 20% per month for a Ni–Cd battery, versus 30% per month for a traditional NiMH under identical conditions), although low self-discharge ("LSD") NiMH batteries are now available, which have substantially lower self-discharge than either Ni–Cd or traditional NiMH batteries.

Environmental impact

Ni–Cd batteries contain between 6% (for industrial batteries) and 18% (for commercial batteries) cadmium, which is a toxic heavy metal and therefore requires special care during battery disposal. In the United States, part of the battery price is a fee for its proper disposal at the end of its service lifetime. Under the so-called "batteries directive" (2006/66/EC), the sale of consumer Ni–Cd batteries has now been banned within the European Union except for medical use; alarm systems; emergency lighting; and portable power tools. This last category has been

banned effective 2016. Under the same EU directive, used industrial Ni–Cd batteries must be collected by their producers in order to be recycled in dedicated facilities.

- Cadmium, being a heavy metal, can cause substantial pollution when discarded in a landfill or incinerated. Because of this, many countries now operate recycling programs to capture and reprocess old batteries.

Nickel Metal Hydride Batteries

A **nickel metal hydride battery**, abbreviated **NiMH** or **Ni–MH**, is a type of rechargeable battery.

The chemical reaction at the positive electrode is similar to that of the nickel–cadmium cell (NiCd), with both using nickel oxide hydroxide (NiOOH).

However, the negative electrodes use a hydrogen-absorbing alloy instead of cadmium.

A NiMH battery can have two to three times the capacity of an equivalent size NiCd, and its energy density can approach that of a lithium-ion battery.

NiMH cells have an alkaline electrolyte, usually potassium hydroxide. The positive electrode is **nickel** hydroxide, and the negative electrode is **hydrogen** in the form of an interstitial **metal hydride**.

History

- Work on NiMH batteries began at the Battelle-Geneva Research Center in 1967
- Interest grew in the 1970s with the commercialization of the nickel–hydrogen battery for satellite applications
- In 1987, Willems and Buschow demonstrated a successful battery with high-energy hybrid alloys incorporating rare-earth metals for the negative electrode (using a mixture of $La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Si_{0.1}$), which kept 84% of its charge capacity after 4000 charge–discharge cycles.
- The first consumer-grade NiMH cells became commercially available in 1989.
- In 1998, Ovonic Battery Co. improved the Ti–Ni alloy structure and composition and patented its innovations
- In 2008, more than two million hybrid cars worldwide were manufactured with NiMH batteries
- About 22% of portable rechargeable batteries sold in Japan in 2010 were NiMH.
- In Switzerland in 2009, the equivalent statistic was approximately 60%. This percentage has fallen over time due to the increase in manufacture of lithium-ion batteries: in 2000, almost half of all portable rechargeable batteries sold in Japan were NiMH.
- In 2015 BASF produced a modified microstructure that helped make NiMH batteries more durable, in turn allowing changes to the cell design that saved considerable weight, allowing the specific energy to reach 140 watt-hours per kilogram.
- Negative electrode reaction occurring in a NiMH cell is
$$H_2O + M + e^- \rightleftharpoons OH^- + MH$$
- On the positive electrode, nickeloxyhydroxide, NiO(OH), is formed:
$$Ni(OH)_2 + OH^- \rightleftharpoons NiO(OH) + H_2O + e^-$$
- The reactions proceed left to right during charge and the opposite during discharge. The metal M in the negative electrode of a NiMH cell is an inter metallic compound

- Many different compounds have been developed for this application, but those in current use fall into two classes. The most common is AB_5, where A is a rare-earth mixture of lanthanum, cerium, neodymium, praseodymium, and B is nickel, cobalt, manganese, or aluminum.
- Some cells use higher-capacity negative electrode materials based on AB_2 compounds, where A is titanium or vanadium, and B is zirconium or nickel, modified with chromium, cobalt, iron, or manganese. Any of these compounds serve the same role, reversibly forming a mixture of metal hydride compounds.
- When overcharged at low rates, oxygen produced at the positive electrode passes through the separator and recombines at the surface of the negative. Hydrogen evolution is suppressed, and the charging energy is converted to heat. This process allows NiMH cells to remain sealed in normal operation and to be maintenance-free

Ni-MH Battery

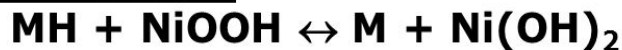cathode: $Ni(OH)_2$
anode: M
Electrolyte: KOH
Reaction at cathode:
  $Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-$
Reaction at anode:
  $M + H_2O + e^- \leftrightarrow MH + OH^-$

Overall Reaction:
  $MH + NiOOH \leftrightarrow M + Ni(OH)_2$

Properties:

➢ Bipolar battery

NiMH batteries of bipolar design (bipolar batteries) are being developed because they offer some advantages for applications as storage systems for electric vehicles. The solid polymer membrane gel separator could be useful for such applications in bipolar design. In other words, this design can help to avoid short-circuits occurring in liquid-electrolyte systems.

➢ Charge

Charging voltage is in the range of 1.4–1.6 V per cell. In general, a constant-voltage charging method cannot be used for automatic charging. When fast-charging, it is advisable to charge the NiMH cells with a smart battery charger to avoid overcharging, which can damage cells

➢ **Trickle charging**

The simplest of the safe charging methods is with a fixed low current, with or without a timer. Most manufacturers claim that overcharging is safe at very low currents, below 0.1 C (C/10) (where C is the current equivalent to the capacity of the battery divided by one hour). The Panasonic NiMH charging manual warns that overcharging for long enough can damage a battery and suggests limiting the total charging time to 10–20 hours.

Panasonic's handbook recommends that NiMH batteries on standby be charged by a lower duty cycle approach, where a pulse of a higher current is used whenever the battery's voltage drops below 1.3 V. This can extend battery life and use less energy.

➢ **ΔV charging method**

In order to prevent cell damage, fast chargers must terminate their charge cycle before overcharging occurs. One method is to monitor the change of voltage with time. When the battery is fully charged, the voltage across its terminals drops slightly. The charger can detect this and stop charging. This method is often used with nickel–cadmium cells, which display a large voltage drop at full charge. However, the voltage drop is much less pronounced for NiMH and can be non-existent at low charge rates, which can make the approach unreliable.

Another option is to monitor the change of voltage with respect to time and stop when this becomes zero, but this risks premature cutoffs. With this method, a much higher charging rate can be used than with a trickle charge, up to 1 C. At this charge rate, Panasonic recommends to terminate charging when the voltage drops 5–10 mV per cell from the peak voltage. Since this method measures the voltage across the battery, a constant-current (rather than a constant-voltage) charging circuit is used.
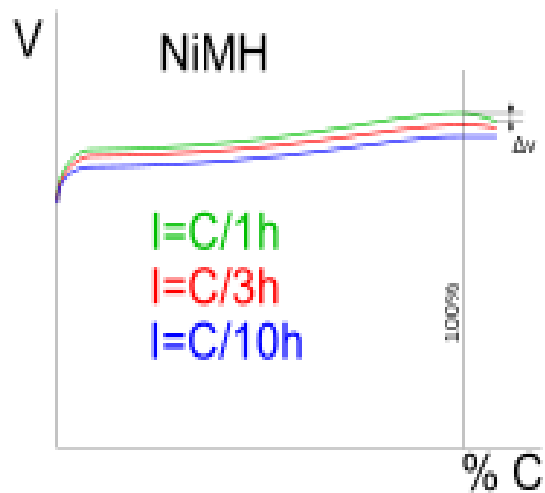
NiMH charge curve

➢ **ΔT charging method**

The temperature-change method is similar in principle to the ΔV method. Because the charging voltage is nearly constant, constant-current charging delivers energy at a near-constant rate. When the cell is not fully charged, most of this energy is converted to chemical energy. However, when the cell reaches full charge, most of the charging energy is converted to heat. This increases the rate of change of battery temperature, which can be detected by a sensor such as a thermistor. Both Panasonic and Duracell suggest a maximal rate of temperature increase of 1 °C per minute. Using a temperature sensor allows an absolute temperature cutoff, which Duracell suggests at 60 °C. With both the ΔT and the ΔV charging methods, both manufacturers recommend a further period of trickle charging to follow the initial rapid charge

➢ **Safety**

A resettable fuse in series with the cell, particularly of the bimetallic strip type, increases safety. This fuse opens if either the current or the temperature gets too high.

Modern NiMH cells contain catalysts to handle gases produced by over-charging ($2H_2+O_2$ _----catalyst--➔ $2H_2O$). However, this only works with overcharging currents of up to 0.1 C (that is, nominal capacity divided by ten hours). This reaction causes batteries to heat, ending the charging process.

A method for very rapid charging called in-cell charge control involves an internal pressure switch in the cell, which disconnects the charging current in the event of overpressure.

One inherent risk with NiMH chemistry is that overcharging causes hydrogen gas to form, potentially rupturing the cell. Therefore, cells have a vent to release the gas in the event of serious overcharging.

NiMH batteries are made of environmentally friendly materials. The batteries contain only mildly toxic substances and are recyclable.

➢ **Loss of capacity**

Voltage depression (often mistakenly attributed to the memory effect) from repeated partial discharge can occur, but is reversible with a few full discharge/charge cycles

➢ **Discharge**

A fully charged cell supplies an average 1.25 V/cell during discharge, declining to about 1.0–1.1 V/cell (further discharge may cause permanent damage in the case of multi-cell packs, due to polarity reversal). Under a light load (0.5 ampere), the starting voltage of a freshly charged AA NiMH cell in good condition is about 1.4

➢ **Over-discharge**

Complete discharge of multi-cell packs can cause reverse polarity in one or more cells, which can permanently damage them. This situation can occur in the common arrangement of four AA cells in series in a digital camera, where one completely discharges before the others due to small differences in capacity among the cells. When this happens, the good cells start to drive the discharged cell into reverse polarity (i.e. positive anode/negative cathode).Some

cameras, GPS receivers and PDAs detect the safe end-of-discharge voltage of the series cells and perform an auto-shutdown, but devices such as flashlights and some toys do not.

Irreversible damage from polarity reversal is a particular danger, even when a low voltage-threshold cutout is employed, when the cells vary in temperature. This is because capacity significantly declines as the cells are cooled. This results in a lower voltage under load of the colder cells.

➢ **Self-discharge**

Historically, NiMH cells have had a somewhat higher self-discharge rate (equivalent to internal leakage) than NiCd cells. The self-discharge rate varies greatly with temperature, where lower storage temperature leads to slower discharge and longer battery life. The self-discharge is 5–20% on the first day and stabilizes around 0.5–4% per day at room temperature. But at 45 °C it is approximately three times as high

➢ **Low self-discharge**

The **low self-discharge nickel metal hydride battery** (**LSD NiMH**) has a significantly lower rate of self-discharge. The innovation was introduced in 2005 by Sanyo, under their Eneloop brand. By using an improved electrode separator and improved positive electrode, manufacturers claim the cells retain 70–85% of their capacity when stored one year at 20 °C (68 °F), compared to about half for normal NiMH batteries. They are otherwise similar to other NiMH batteries and can be charged in typical NiMH chargers. These cells are marketed as "hybrid", "ready-to-use" or "pre-charged" rechargeable

Retention of charge depends in large part on the battery's leakage resistance (the higher the better), and on its physical size and charge capacity.

Separators keep the two electrodes apart to slow electrical discharge while allowing the transport of ionic charge carriers that close the circuit during the passage of current. High-quality separators are critical for battery performance.

Thick separators are one way to reduce self-discharge, but take up space and reduce capacity, while thin separators tend to raise the self-discharge rate. Some batteries may have overcome this tradeoff using thin separators with more precise manufacturing and by using a sulfonated polyolefin separator, a further improvement over the hydrophilic polyolefin based on ethylene vinyl alcohol.

Low-self-discharge cells have lower capacity than standard NiMH cells because of the separator's larger volume. The highest-capacity low-self-discharge AA cells have 2500 mAh capacity, compared to 2700 mAh for high-capacity AA NiMH cells.

➢ <u>**Compared to other battery types**</u>

NiMH cells are often used in digital cameras and other high-drain devices, where over the duration of single-charge use they outperform primary (such as alkaline) batteries. NiMH

cells are advantageous for high-current-drain applications, largely due to their lower internal resistance.

Typical alkaline AA-size batteries, which offer approximately 2600 mAh capacity at low current demand (25 mA), provide only 1300 mAh capacity with a 500 mA load. Digital cameras with LCDs and flashlights can draw over 1000 mA, quickly depleting them. NiMH cells can deliver these current levels without similar loss of capacity.

Low internal resistance allows NiMH cells to deliver a nearly constant voltage until they are almost completely discharged. Thus battery-level indicators designed to read alkaline cells overstate the remaining charge when used with NiMH cells, as the voltage of alkaline cells decreases steadily during most of the discharge cycle.

Lithium-ion batteries have a higher specific energy than nickel metal hydride batteries, but they are significantly more expensive. They also produce a higher voltage (3.2-3.7V nominal), and are thus not a drop-in replacement for alkaline batteries without circuitry to reduce voltage.

As of 2005, nickel metal hydride batteries constituted three percent of the battery market.

Applications:
Consumer electronics

NiMH batteries have replaced NiCd for many roles, notably small rechargeable batteries. NiMH batteries are commonly available in AA (penlight-size) batteries. These have nominal charge capacities (C) of 1.1–2.8 Ah at 1.2 V, measured at the rate that discharges the cell in 5 hours. Useful discharge capacity is a decreasing function of the discharge rate, but up to a rate of around $1 \times C$ (full discharge in 1 hour), it does not differ significantly from the nominal capacity. NiMH batteries nominally operate at 1.2 V per cell, somewhat lower than conventional 1.5 V cells, but can operate many devices designed for that voltage.

Electric vehicles
Main articles: Electric vehicle, Battery electric vehicle

Prior all-electric plug-in vehicles included the General Motors EV1, first-generation Toyota RAV4 EV, Honda EV Plus, Ford Ranger EV and Vectrix scooter. Every first generation hybrid vehicle used NIMH batteries, most notably the Toyota Prius and Honda Insight, as well as later models including the Ford Escape Hybrid, Chevrolet Malibu Hybrid and Honda Civic Hybrid also use them.

Example battery:

Properties of Modern NiMH rechargeable cells	
Specific energy	60–120 W·h/kg
Energy density	140–300 W·h/L
Specific power	250–1,000 W/kg
Charge/discharge efficiency	66%–92%
Self-discharge rate	13.9–70.6% at room temperature 36.4–97.8% at 45 °C Low self-discharge: 0.08–2.9% (per month)
Cycle durability	180–2000 cycles
Nominal cell voltage	1.2 V

Lithium Ion batteries

Brief History:

A **lithium-ion battery** or **Li-ion battery** (abbreviated as **LIB**) is a type of rechargeable battery. Lithium-ion batteries are commonly used for portable electronics and electric vehicles and are growing in popularity for military and aerospace applications.

A prototype Li-ion battery was developed by Akira Yoshino in 1985, based on earlier research by John Goodenough, M. Stanley Whittingham, Rachid Yazami and Koichi Mizushima during the 1970s–1980s, and then a commercial Li-ion battery was developed by a Sony and Asahi Kasei team led by Yoshio Nishi in 1991.

In 2019, The Nobel Prize in Chemistry was given to Yoshino, Goodenough, and Whittingham "for the development of lithium ion batteries"

Construction:

The three primary functional components of a lithium-ion battery are the positive and negative electrodes and electrolyte. Generally, the negative electrode of a conventional lithium-ion cell is made from carbon. The positive electrode is typically a metal oxide. The electrolyte is lithium salt in an organic solvent. The electrochemical roles of the electrodes reverse between anode and cathode, depending on the direction of current flow through the cell.

The most commercially popular anode (negative electrode) is graphite. The positive electrode is generally one of three materials: a layered oxide (such as lithium cobalt oxide), a polyanion (such as lithium iron phosphate) or a spinel (such as lithium manganese oxide). Recently, graphene containing electrodes (based on 2D and 3D structures of graphene) have also been used as components of electrodes for lithium batteries.

The electrolyte is typically a mixture of organic carbonates such as ethylene carbonate or diethyl carbonate containing complexes of lithium ions. These non-aqueous electrolytes generally use non-coordinating anion salts such as lithium hexafluorophosphate($LiPF_6$), lithium hexafluoroarsenate monohydrate($LiAsF_6$), lithium perchlorate($LiClO_4$), lithium tetrafluoroborate ($LiBF_4$), and lithium triflate ($LiCF_3SO_3$).

Depending on materials choices, the voltage, energy density, life, and safety of a lithium-ion battery can change dramatically. Current effort has been exploring the use of novel architectures using nanotechnology have been employed to improve performance. Areas on interest include nano-scale electrode materials and alternative electrode structures.[

Pure lithium is highly reactive. It reacts vigorously with water to form lithium hydroxide($LiOH$) and hydrogen gas. Thus, a non-aqueous electrolyte is typically used, and a sealed container rigidly excludes moisture from the battery pack.

Lithium-ion batteries are more expensive than NiCd batteries but operate over a wider temperature range with higher energy densities. They require a protective circuit to limit the peak voltage.

The battery pack of a laptop computer, for each lithium-ion cell, will contain

- a temperature sensor
- a voltage regulator circuit
- a voltage tap
- a charge-state monitor
- a mains connector

These components

- monitor the charge-state and current flow
- record the latest, full-charge capacity
- monitor the temperature

- **Charge and discharge**

During discharge, lithium ions (Li^+) carry the current within the battery from the negative to the positive electrode, through the non-aqueous electrolyte and separator diaphragm.

During charging, an external electrical power source (the charging circuit) applies an over-voltage (a higher voltage than the battery produces, of the same polarity), forcing a charging current to flow **within the battery** from the positive to the negative electrode, i.e. in the reverse direction of a discharge current under normal conditions. The lithium ions then migrate from the positive to the negative electrode, where they become embedded in the porous electrode material in a process known as intercalation.

Energy losses arising from electrical contact resistance at interfaces between electrode layers and at contacts with current-collectors can be as high as 20% of the entire energy flow of batteries under typical operating conditions.
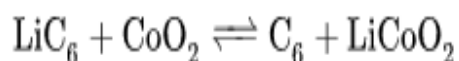
Electrochemistry

The positive electrode (cathode) half-reaction in the lithium-doped cobalt oxide substrate is

$$CoO_2 + Li^+ + e^- \rightleftharpoons LiCoO_2$$
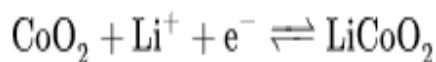
The negative electrode (anode) half-reaction for the graphite is

$$LiC_6 \rightleftharpoons C_6 + Li^+ + e^-$$
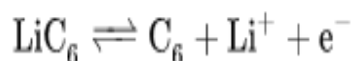
The full reaction (left to right: discharging, right to left: charging) being

$$LiC_6 + CoO_2 \rightleftharpoons C_6 + LiCoO_2$$
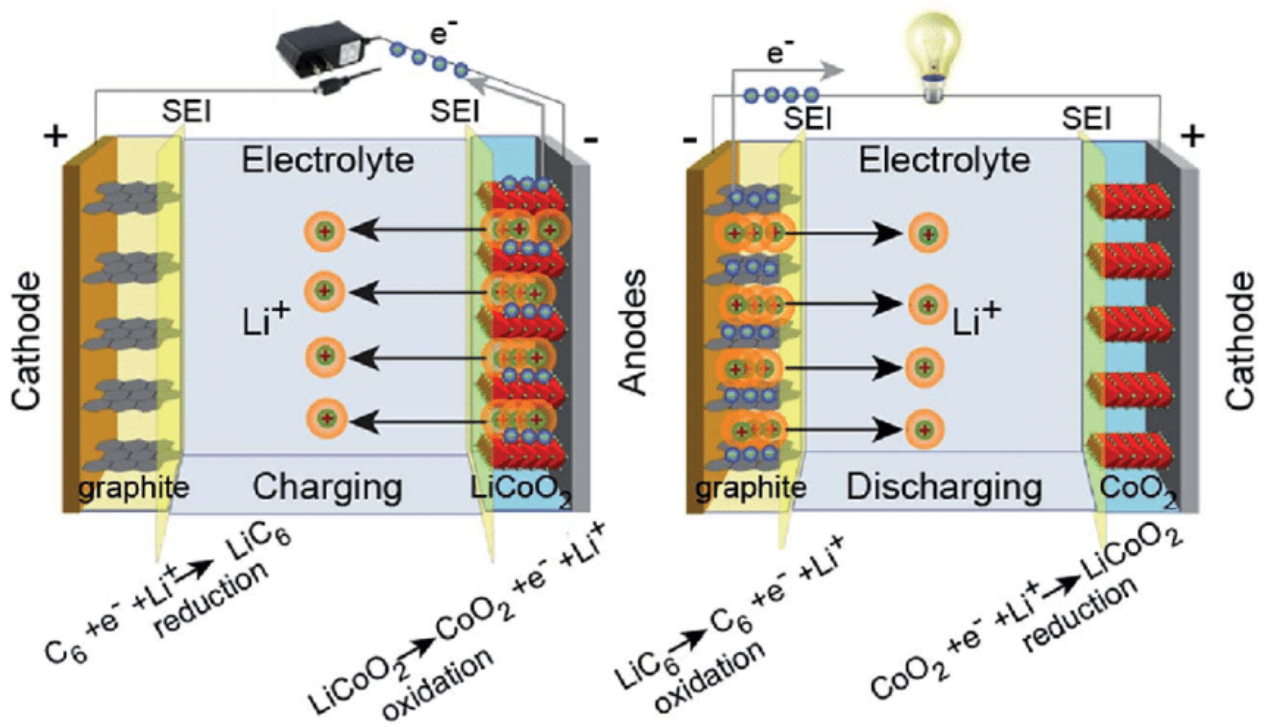
The **charging procedures** for Li-ion batteries:

- **Constant current**

The charger applies a constant current to the battery at a steadily increasing voltage, until the voltage limit per cell is reached.

- **Balance (not required once a battery is balanced)**

The charger reduces the charging current (or cycles the charging on and off to reduce the average current) while the state of charge of individual cells is brought to the same level by a balancing circuit, until the battery is balanced

- **Constant voltage**

The charger applies a voltage equal to the maximum cell voltage times the number of cells in series to the battery, as the current gradually declines towards 0, until the current is below a set threshold of about 3% of initial constant charge current.

Advantages

- High energy density - potential for yet higher capacities.
- Does not need prolonged priming when new. One regular charge is all that's needed.
- Relatively low self-discharge - self-discharge is less than half that of nickel-based batteries.
- Low Maintenance - no periodic discharge is needed; there is no memory. Specialty cells can provide very high current to applications such as power tools.

Limitations

- Requires protection circuit to maintain voltage and current within safe limits.
- Subject to aging, even if not in use - storage in a cool place at 40% charge reduces the aging effect.
- Transportation restrictions - shipment of larger quantities may be subject to regulatory control. This restriction does not apply to personal carry-on batteries.
- Expensive to manufacture - about 40 percent higher in cost than nickel-cadmium.
- Not fully mature - metals and chemicals are changing on a continuing basis.

Different types of Lithium ion Batteries				
Technology (Positive electrode)	**Company**	**Target application**	**Date**	**Benefit**
Lithium Cobalt Oxide ($LiCoO_2$, "LCO")	Sony first commercial production	broad use, laptop	1991	High specific energy
Lithium Iron Phosphate ("LFP", $LiFePO_4$)	University of Texas/Hydro-Québec, Phostech Lithium Inc., Valence Technology, A123Systems/MIT	Segway Personal Transporter, power tools, aviation products, automotive hybrid systems, PHEV conversions	1996	Moderate density (2 A·h outputs 70 amperes) High safety compared to Cobalt / Manganese systems. Operating temperature >60 °C (140 °F)
Lithium Manganese Oxide ("LMO", LiMn2O4)	LG Chem, NEC, Samsung, Hitachi, Nissan/AESC, EnerDel	Hybrid electric vehicle, cell phone, laptop	1996	
Lithium Nickel Cobalt Aluminium Oxide ("NCA", LiNiCoAlO2)	Panasonic, Saft Groupe S.A. Samsung	Electric vehicles	1999	High specific energy, Good life span
Lithium nickel manganese cobalt oxide ("NMC", LiNixMnyCozO2)	Imara Corporation, Nissan Motor, Microvast Inc., LG Chem, Northvolt	Electric vehicles, power tools, grid energy storage	2008	Good specific energy and Specific power density

Example:

A Li-ion battery from a Nokia 3310 mobile phone	
Specific energy	100–265 W·h/kg (0.36–0.875 MJ/kg)
Energy density	250–693 W·h/L (0.90–2.43 MJ/L)
Specific power	~250 – ~340 W/kg
Charge/discharge efficiency	80–90%
Energy/consumer-price	6.4Wh/US$
Self-discharge rate	0.35% to 2.5% per month depending on state of charge
Cycle durability	400–1,200 cycles
Nominal cell voltage	3.6 / 3.7 / 3.8 / 3.85 V, LiFePO4 3.2 V