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Batteries, Flywheels and Supercapacitors

3.1 Introduction

We have seen in the previous chapter that there are many different types and sizes of EVs. However, in nearly all road vehicles the battery is a key component. In the classical EV the battery is the only energy store, and the component with the highest cost, weight and volume. In hybrid vehicles the battery, which must continually accept and give out electrical energy, is also a key component of the highest importance. Some fuel cell (FC) vehicles have been made which have batteries that are no larger than those normally fitted to IC engine cars, but it is probably that most early FC-powered vehicles will have quite large batteries and work in hybrid FC/battery mode. In short, a good understanding of battery technology and performance is vital to anyone involved with electric road vehicles.

What is an electric battery? A battery consists of two or more electric cells connected together. The cells convert chemical energy to electrical energy. The cells consist of positive and negative electrodes in an electrolyte. It is the chemical reaction between the electrodes and the electrolyte which generates DC electricity. In the case of secondary or rechargeable batteries the chemical reaction can be reversed by reversing the current and the battery returned to a charged state.

The 'lead acid' battery is the traditional rechargeable type, but there are others which are becoming popular in modern EVs. The first EV using rechargeable batteries preceded the invention of the rechargeable lead acid battery by a quarter of a century, and there are a very large number of materials and electrolytes that can be combined to form a battery. However, only a relatively small number of combinations have been developed as commercial rechargeable electric batteries suitable for use in vehicles. At present these include lead acid, nickel iron, nickel cadmium, nickel metal hydride (NiMH), lithium polymer and lithium iron, sodium sulfur and sodium metal chloride. There are also more recent developments of batteries that can be mechanically refuelled, the main ones being aluminium–air and zinc–air. Despite all the different possibilities tried, and

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about 150 years of development, a suitable battery has only recently been developed which allows mass production of EVs.

From the EV designer's point of view the battery can be treated as a 'black box' that has a range of performance criteria. These criteria will include specific energy, energy density, specific power, typical voltages, amphour efficiency, energy efficiency, commercial availability, cost, operating temperatures, self-discharge rates, number of life cycles and recharge rates – terms which will be explained in the following section. The designer also needs to understand how energy availability varies with ambient temperature, charge and discharge rates, battery geometry, optimum temperature, charging methods, cooling needs and likely future developments. However, at least a basic understanding of the battery chemistry is very important, otherwise the performance and maintenance requirements of the different types, and most of the disappointments connected with battery use, such as their limited life, self-discharge, reduced efficiency at higher currents, and so on, cannot be understood. This basic knowledge is also needed in regard to likely hazards in an accident and the overall impact of the use of battery chemicals on the environment. Recycling of used batteries is also becoming increasingly important.

The main parameters that specify the behaviour and performance of a battery are given in the following section. In the later sections the chemistry and performance of the most important battery types are outlined, and finally the very important topic of battery performance modelling is outlined.

3.2 Battery Parameters

3.2.1 Cell and Battery Voltages

All electric cells have nominal voltages which give the approximate voltage when the cell is delivering electrical power. The cells can be connected in series to give the overall voltage required. Traction batteries for EVs are usually specified as 6 V or 12 V, and these units are in turn connected in series to produce the voltage required. This voltage will, in practice, change. When a current is given out, the voltage will fall; on charging, the voltage will rise.

This is best expressed in terms of 'internal resistance' and the equivalent circuit of a battery shown in Figure 3.1. The battery is represented as having a fixed voltage E, but the voltage at the terminals is a different voltage V, because of the voltage across the internal resistance R. Assuming that a current I is flowing out of the battery, as in Figure 3.1, then by basic circuit theory we can say that

$$V = E - IR \tag{3.1}$$

Note that if the current I is zero, the terminal voltage is equal to E, and so E is often referred to as the open-circuit voltage. If the battery is being charged, then clearly the voltage will *increase* by *IR*. In EV batteries the internal resistance should clearly be as low as possible.¹

Generally Equation (3.1) gives a fairly good prediction of the 'in-use' battery voltage. However, the open-circuit voltage E is not in fact constant. The voltage is also affected by

¹ A good-quality 12 V, 25 Ah lead acid battery will typically have an internal resistance of about 0.005 Ω .



Figure 3.1 Simple equivalent circuit model of a battery. This battery is composed of six cells

the 'state of charge' and other factors such as temperature. This is dealt with in more detail in Section 3.12, where we address the problem of modelling the performance of batteries.

3.2.2 Charge (or Amphour) Capacity

The electric charge that a battery can supply is clearly a most crucial parameter. The SI unit for this is the coulomb – the charge when 1 A flows for 1 second. However, this unit is inconveniently small. Instead the amphour is used – 1 A flowing for 1 hour. The capacity of a battery might be, say, '10 Ah'. This means that it can provide 1 A for 10 hours, or 2 A for 5 hours, or, in theory, 10 A for 1 hour. However, in practice, it does not work out like this for most batteries.

It is usually the case that while a battery may be able to provide 1 A for 10 hours, if 10 A is drawn from it, it will last less than 10 hours. It is most important to understand this. The capacity of the large batteries used in EVs ('traction batteries') is usually quoted for a 5 hour discharge. Figure 3.2 shows how the capacity is affected if the charged is removed more quickly, or more slowly. The diagram is for a nominally 100 Ah battery. Notice that if the charge is removed in 1 hour, the capacity falls very considerably to about 70 Ah. On the other hand, if the current is drawn off more slowly, in say 20 hours, the capacity rises to about 110 Ah.

This change is capacity occurs because of unwanted side reactions inside the cell. The effect is most noticeable in the lead acid battery, but occurs in all types. It is very important to be able to predict accurately the effects of this phenomenon, and this is addressed in Section 3.12, when we consider battery modelling.

The charge capacity leads to an important notational point that should be explained here. The capacity of a battery in amphours is represented by the letter C. However, somewhat confusingly, till you get used to it, this is also used to represent a current.

Suppose a battery has a capacity of 42 Ah; then it is said that C = 42 A. Battery users talk about 'a discharge current of 2C', or 'charging the battery at 0.4C'. In these cases this would mean a 'discharge current of 84 A', or a 'charging current of 16.8 A'.

A further refinement is to use a subscript with the C symbol. As we noted above, the amphour capacity of a battery varies with the time taken for the discharge. In our example, the 42 Ah battery is rated thus for a 10 hour discharge. In this more complete notation, a discharge current of 84 A should be written as $2C_{10}$.



Figure 3.2 Graph showing the change is amphour charge capacity of a nominally 42 Ah battery. This graph is based on measurements from a lead acid traction battery produced by Hawker Energy Products Inc.

Example: Express the current 21 A from our example 42 Ah battery in 'C' notation. As a ratio of 42 A, 21 is 1/2 or 0.5. Thus the current 21 A = $0.5C_{10}$.

This way of expressing a battery current is very useful, as it relates the current to the size of the battery. It is almost universally used in the battery literature and specifications, though the subscript relating to the rated discharge time is often omitted.

3.2.3 Energy Stored

The purpose of the battery is to store energy. The energy stored in a battery depends on its *voltage* and the *charge* stored. The SI unit is the joule, but this is an inconveniently small unit, and so we use the watthour instead. This is the energy equivalent of working at a power of 1 W for 1 hour. The watthour is equivalent to 3600 J. The watthour is compatible with our use of the amphour for charge, as it yields the simple formula

Energy in watthours = voltage
$$\times$$
 amphours, or Energy = $V \times C$ (3.2)

However, this equation must be used with great caution. We have noted that both the battery voltage V and even more so the ampere hour capacity C vary considerably depending on how the battery is used. Both are reduced if the current is increased and the battery is drained quickly. The stored energy is thus a rather variable quantity and reduces if the energy is released quickly. It is usually quoted in line with the amphour rating; that

is, if the charge capacity is given for a 5 hour discharge, then the energy should logically be given for this discharge rate.

3.2.4 Specific Energy

Specific energy is the amount of electrical energy stored for every kilogram of battery mass. It has units of $Wh kg^{-1}$. Once the energy capacity of the battery needed in a vehicle is known (watthours) it can be divided by the specific energy ($Wh kg^{-1}$) to give a first approximation of the battery mass. Specific energies quoted can be no more than a guide, because, as we have seen, the energy stored in a battery varies considerably with factors such as temperature and discharge rate.

We will see in Section 3.2.6, and in the Ragone plot of Figure 3.3, how much the specific energy of a battery can change.

3.2.5 Energy Density

Energy density is the amount of electrical energy stored per cubic metre of battery volume. It normally has units of $Wh m^{-3}$. It is also an important parameter as the energy capacity of the battery (Wh) can be divided by its energy density (Wh m⁻³) to show the volume of battery required. Alternatively, if a known volume is available for batteries, the volume (m³) can be multiplied by the battery's energy density (Wh m⁻³) to give a



Figure 3.3 A 'Ragone plot' – specific power against specific energy graph – for typical lead acid and nickel cadmium traction batteries

first approximation of how much electrical energy can be made available. The battery volume may well have a considerable impact on vehicle design. As with specific energy, the energy density is a nominal.

3.2.6 Specific Power

Specific power is the amount of power obtained per kilogram of battery. It is a highly variable and rather anomalous quantity, since the power given out by the battery depends far more upon the load connected to it than the battery itself. Although batteries do have a maximum power, it is not sensible to operate them at anywhere near this maximum power for more than a few seconds, as they will not last long and would operate very inefficiently.

The normal units are $W kg^{-1}$. Some batteries have a very good specific energy, but have low specific power – which means they store a lot of energy, but can only give it out slowly. In EV terms, they can drive the vehicle very slowly over a long distance. High specific power normally results in lower specific energy for any particular type of battery. This is because, as we saw in Section 3.2.2, taking the energy out of a battery quickly, that is at high power, reduces the energy available.

This difference in change of specific power with specific energy for different battery types is very important, and it is helpful to be able to compare them. This is often done using a graph of specific power against specific energy, which is known as a 'Ragone plot'. Logarithmic scales are used, as the power drawn from a battery can vary greatly in different applications. A Ragone plot for a good-quality lead acid traction battery, and a similar NiCad battery, is shown in Figure 3.3.

It can be seen that, for both batteries, as the specific power increases, the specific energy is reduced. In the power range $1-100 \text{ W kg}^{-1}$ the NiCad battery shows slightly less change. However, above about 100 W kg^{-1} the NiCad battery falls much faster than the lead acid.

Ragone plots like Figure 3.3 are used to compare energy sources of all types. In this case we should conclude that, ignoring other factors such as cost, the NiCad battery performs better if power densities of less than 100 W kg^{-1} are required. However, at higher values, up to 250 W kg^{-1} or more, then the lead acid begins to become more attractive. The Ragone plot also emphasises the point that a simple single-number answer cannot be given to the question 'What is the specific power of this battery?'

3.2.7 Amphour (or Charge) Efficiency

In an ideal world a battery would return the entire charge put into it, in which case the amphour efficiency is 100%. However, none do! Their charging efficiency is less than 100%. The precise value will vary with different types of battery, temperature and rate of charge. It will also vary with the state of charge. For example, when charged from about 20-80% charged the efficiency will usually be very close to 100%, but as the last 20% of the charge is put in the efficiency falls off greatly. The reasons for this will be made clear when we look at each of the battery types later in the chapter.

3.2.8 Energy Efficiency

This is another very important parameter and it is defined as the ratio of electrical energy supplied by a battery to the amount of electrical energy required to return it to the state before discharge. A strong argument for using EVs is based on the efficient use of energy, with a resulting reduction of overall emissions – hence high energy efficiency is desirable. It should be clear from what has been said in the preceding sections that the energy efficiency will vary very greatly with how a battery is used. If the battery is charged and discharged rapidly, for example, energy efficiency decreases considerably. However, it does act as a guide for comparing batteries, in much the same way as fuel consumption does for cars.

3.2.9 Self-discharge Rates

Most batteries discharge when left unused, and this is known as self-discharge. This is important as it means some batteries cannot be left for long periods without recharging. The reasons for this self-discharge will be explained in the sections that follow. The rate varies with battery type and with other factors such as temperature – higher temperatures greatly increase self-discharge.

3.2.10 Battery Geometry

Cells come in many shapes: round, rectangular, prismatic or hexagonal. They are normally packaged into rectangular blocks. Some batteries can be supplied with a fixed geometry only. Some can be supplied in a wide variation of heights, widths and lengths. This can give the designer considerable scope, especially when starting with a blank sheet of paper – or more likely today a blank CAD screen. The designer could, for example, spread the batteries over the whole floor area ensuring a low centre of gravity and very good handling characteristics.

3.2.11 Battery Temperature, Heating and Cooling Needs

While most batteries run at ambient temperature, some run at higher temperatures and need heating to start with and then cooling when in use. In others, battery performance drops off at low temperatures, which is undesirable, though this problem could be overcome by heating the battery. When choosing a battery the designer needs to be aware of battery temperature, heating and cooling needs and has to take these into consideration during the vehicle design process.

3.2.12 Battery Life and Number of Deep Cycles

Most rechargeable batteries will only undergo a few hundred deep cycles to 20% of the battery charge. However, the exact number depends on the battery type, and also on the details of the battery design and on how the battery is used. This is a very important figure

in a battery specification, as it reflects the lifetime of the battery, which in turn reflects the EV running costs. More specific information about this, and all the other battery parameters mentioned, are given in the sections that follow on particular battery types.

3.3 Lead Acid Batteries

3.3.1 Lead Acid Battery Basics

Until recently the best known and most widely used battery for EVs is the lead acid battery. Lead acid batteries are widely used for starting IC engine vehicles and as such are well known. However, for EVs, more robust lead acid batteries that withstand deep cycling and use a gel rather than a liquid electrolyte are used. These batteries are more expensive to produce.

In the lead acid cells the negative plates have a spongy lead as their active material, while the positive plates have an active material of lead dioxide. The plates are immersed in an electrolyte of dilute sulfuric acid. The sulfuric acid combines with the lead and the lead oxide to produce lead sulfate and water, electrical energy being released during the process. The overall reaction is

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

The reactions on each electrode of the battery are shown in Figure 3.4. In the upper diagram the battery is discharging. Both electrode reactions result in the formation of lead sulfate. The electrolyte gradually loses the sulfuric acid, and becomes more dilute.

When being charged, as in the lower diagram of Figure 3.4, the electrodes revert to lead and lead dioxide. The electrolyte also recovers its sulfuric acid, and the concentration rises.

The lead acid battery is the most commonly used rechargeable battery in anything but the smallest of systems. The main reasons for this are that the main constituents (lead, sulfuric acid, a plastic container) are not expensive, that it performs reliably, and that it has a comparatively high voltage of about 2 V per cell. The overall characteristics of the battery are given in Table 3.1.

One of the most notable features of the lead acid battery is its extremely low internal resistance (see Section 3.2.1 and Figure 3.1). This means that the fall in voltage as current is drawn is remarkably small – probably smaller than for any of the candidate vehicle batteries. The figure given in Table 3.1 is for a single cell, of nominal capacity 1.0 Ah. The capacity of a cell is approximately proportional to the area of the plates, and the internal resistance is approximately inversely proportional to the plate area. The result is that the internal resistance is, to a good approximation, inversely proportional to the capacity. The figure given in Table 3.1 of 0.022Ω per cell is a rule of thumb taken from a range of good-quality traction batteries. A good estimate of the internal resistance of a lead acid battery is thus

$$R = \text{no. of cells} \times \frac{0.022}{C_{10}}\Omega$$
(3.3)

The number of cells is the nominal battery voltage divided by 2.0, that is six in the case of a 12 V battery. C_{10} is the amphour capacity at the 10 h rate.



 $\begin{array}{c} \textbf{PbSO}_4 \ + \ 2e^- \ \rightarrow \ \textbf{Pb} \ + \ \textbf{SO}_4^{2^-} \\ \textbf{2H}_2\textbf{O} \ \rightarrow \ \textbf{4H}^+ \ \textbf{2O}^{2^-}; \ \textbf{4H}^+ \ \textbf{2SO}_4^{2^-} \ \rightarrow \ \textbf{2H}_2\textbf{SO}_4 \\ \textbf{DC supply} \\ \textbf{+} \\ \textbf{PbSO}_4 \ + \ \textbf{2O}^2 \ \rightarrow \ \textbf{PbO}_2 \ + \ \textbf{SO}_4^2 \ + \ \textbf{2e}^- \\ \textbf{Negative electrode changes back} \\ from lead sulfate to lead peroxide \\ \end{array}$

Reaction during the **charging** of the lead acid battery. Note that the electrolyte sulfuric acid concentration increases.



 Table 3.1
 Nominal battery parameters for lead acid batteries

Specific energy	$20-35 \text{ Wh kg}^{-1}$ depending on usage
Energy density	$54-95 \mathrm{Wh}\mathrm{l}^{-1}$
Specific power	$\sim 250 \mathrm{W kg^{-1}}$ before efficiency falls very greatly
Nominal cell voltage	2 V
Amphour efficiency	\sim 80%, varies with rate of discharge and temperature
Internal resistance	Extremely low, $\sim 0.022 \Omega$ per cell for 1 Ah cell
Commercially available	Readily available from several manufacturers
Operating temperature	Ambient, poor performance in extreme cold
Self discharge	$\sim 2\%$ per day (but see text)
Number of life cycles	Up to 800 to 80% capacity
Recharge time	8 h (but 90% recharge in 1 h possible)

3.3.2 Special Characteristics of Lead Acid Batteries

Unfortunately the lead acid battery reactions shown in Equation (3.4) are not the only ones that occur. The lead and lead dioxide are not stable in sulfuric acid and decompose, albeit very slowly, with the reactions:

At the positive electrode: $2 PbO_2 + 2 H_2SO_4 \rightarrow 2 PbSO_4 + 2 H_2O + O_2$ (3.4)

At the negative electrode: $Pb + H_2SO_4 \rightarrow PbSO_4 + H_2$ (3.5)

This results in the self-discharge of the battery. The rate at which these reactions occur depends on the temperature of the cell – faster if hotter. It also depends on other factors, such as the purity of the components (hence quality) and the precise alloys used to make up the electrode supports.

These unwanted reactions, which also produce hydrogen and oxygen gas, also occur while the battery is discharging. In fact they occur faster if the battery is discharged faster, due to lower voltage, higher temperature and higher electrode activity. This results in the 'lost charge' effect that occurs when a battery is discharged more quickly, and which was noted in Section 3.2.2 above. It is a further unfortunate fact that these discharge reactions will not occur at exactly the same rate in all the cells, and thus some cells will become more discharged than others. This has very important consequences for the way batteries are charged, as explained below. But, in brief, it means that some cells will have to tolerate being 'overcharged' to make sure all the cells become charged.

The reactions that occur in the lead acid battery when it is being 'overcharged' are shown in Figure 3.5. These 'gassing' reactions occur when there is no more lead sulfate on the electrodes to give up or accept the electrons. They thus occur when the battery is fully or nearly fully charged.

We have noted that the charging and discharging reactions (as in Figure 3.4) involve changing the concentration of the electrolyte of the cells. The change in concentration of the reactants means that there is a small change in the voltage produced by the cell as it



Figure 3.5 The 'gassing' reactions that occur when the lead acid battery is fully charged



Figure 3.6 Graph showing how the open-circuit voltage of a sealed lead acid battery changes with state of charge

discharges. This decline in voltage is illustrated in Figure 3.6. For modern sealed batteries the change is linear to quite a good approximation. It should be noted that this battery voltage *cannot* normally be used to give an indication of the state of charge of the battery. It is not normally possible to measure this open-circuit voltage when the battery is in use, and in any case it is also greatly affected by temperature, so a chance measurement of the battery voltage is likely to be strongly affected by other factors.

A notable feature of the overcharge reactions of Figure 3.5 and the self-discharge reactions of Equations (3.4) and (3.5) is that water is lost and turned into hydrogen and oxygen. In older battery designs this gas was vented out and lost, and the electrolyte had to be topped up from time to time with water. In modern sealed batteries this is not necessary or even possible. The gases are trapped in the battery and allowed to recombine (which happens at a reasonable rate spontaneously) to reform as water. Clearly there is a limit to the rate at which this can happen, and steps must be taken to make sure gas is not produced too rapidly. This is dealt with in the sections that follow.

Manufacturers of lead acid batteries can supply them in a wide range of heights, widths and lengths, so that for a given required volume they can be fairly accommodating. However, a problem with the wide use of lead acid batteries is that different designs are made for different applications, and it is essential to use the correct type. The type of battery used for the conventional car, the so-called starting, lighting and ignition (SLI) battery, is totally unsuitable for EV applications. Other lead acid batteries are designed for occasional use in emergency lighting and alarms – these are also totally unsuitable. The difference in manufacture is dealt with in publications such as Vincent and Scrosati (1997). It is only batteries of the 'traction' or 'deep cycling' type that are suitable here. These are the most expensive type of lead acid battery.

3.3.3 Battery Life and Maintenance

We have seen that gassing reactions occur within the lead acid battery, leading to loss of electrolyte. Traditional acid batteries require topping up with distilled water from time to time, but modern vehicle lead acid batteries are sealed to prevent electrode loss. In addition the electrolyte is a gel, rather than liquid. This means that maintenance of the electrolyte is no longer needed. However, the sealing of the battery is not total: there is a valve which releases gas at a certain pressure, and if this happens the water loss will be permanent and irreplaceable. This feature is a safety requirement and leads to the name 'valve-regulated sealed lead acid' (VRLA) for this modern type of battery. Such buildup of gas will result if the reactions of Figure 3.5, which occur on overcharge, proceed too fast. This will happen if the charging voltage is too high. Clearly this must not be allowed to happen, or the battery will be damaged. On the positive side, it means that such batteries are essentially 'maintenance free'.

However, this does not mean that the batteries will last for ever. Even if there is no water loss, lead acid batteries are subject to many effects that shorten their life. One of the most well known is the process called 'sulfation'. This occurs if the battery is left for a long period (i.e. 2 weeks or more) in a discharged state. The lead sulfate (see Figure 3.4) on the electrodes forms into larger crystals, which are harder to convert back into lead or lead dioxide, and which form an insulating layer over the surface of the electrodes. By slowly recharging the battery this can sometimes be partially reversed, but often it cannot.

Making sure the battery is always kept in a good state of charge can prevent the problem of sulfation – and this is explained in Section 3.8. Section 3.8 also explains the very important issue of charge equalisation – getting this wrong is a major cause of battery failure. Other problems cannot be prevented however much care is taken. Within the electrodes of the battery corrosion reactions take place, which increases the electrical resistance of the contacts between the active materials that the electrode supports. The active materials will gradually form into larger and larger crystals, which will reduce the surface area, both reducing the capacity of the battery and slowing down the rate of reaction. The effects of vibration and the continual change of size of the active materials during the charge/discharge cycles (see Figure 3.4) will gradually dislodge them. As a result they will not make such good electrical contact with their support, and some will even fall off and become completely detached.

All these problems mean that the life of the lead acid battery is limited to around 700 cycles, though this strongly depends on the depth of the cycles. Experience with industrial trucks (fork-lifts, luggage carriers at railway stations, etc.) suggests that service lives of 1200-1500 cycles are possible, over 7-8 years. Fleet experience with electric cars indicates a life of about 5 years or 700 cycles. The shorter life of the road vehicles is the result of much greater battery load, the battery typically being discharged in about 2 hours, as opposed to the 7-8 hours for industrial trucks.

3.3.4 Battery Charging

Charging a lead acid battery is a complex procedure and, as with any battery, if carried out incorrectly it will quickly ruin the battery and decrease its life. As we have seen, the charging must not be carried out at too high a voltage, or water loss results.

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There are differing views on the best way of charging lead acid batteries and it is essential that, once a battery is chosen, the manufacturer's advice is sought.

The most commonly used technique for lead acid batteries is called multiple step charging. In this method the battery is charged until the cell voltage is raised to a predetermined level. The current is then switched off and the cell voltage is allowed to decay to another predetermined level, and then the current is switched on again. A problem is that the predetermined voltages vary depending on the battery type, but also on the temperature. However, the lead acid battery is used in so many applications that suitable good-quality chargers are available from a wide range of suppliers.

An important point that applies to all battery types relates to the process of 'charge equalisation' that must be done in all batteries at regular intervals if serious damage is not to result. It is especially important for lead acid batteries. This is fully explained below in Section 3.9, after all the main battery types have been described.

3.3.5 Summary of Lead Acid Batteries

Lead acid batteries are well established commercially with good backup from industry. They are the cheapest rechargeable batteries per kilowatt-hour of charge, and will remain so for the foreseeable future. However, they have low specific energy and it is hard to see how a long-range vehicle can be designed using a lead acid battery. Lead acid will undoubtedly continue to be widely used for some considerable time in short-range vehicles. Lead acid batteries have a greater range of efficient specific powers than many other types (see Figure 3.3) and so they are very much in contention in hybrid EVs, where only a limited amount of energy is stored, but it should be taken in and given out quickly.

3.4 Nickel-Based Batteries

3.4.1 Introduction

A range of commercial batteries, using nickel in the positive electrode, have been developed since Edison's work in the late nineteenth century. These batteries include nickel iron, nickel zinc, nickel cadmium and NiMH batteries. Three of these batteries are discussed below, the NiMH battery showing the most promise. The nickel zinc battery has a reasonable performance but it has a very limited life of 300 deep cycles and is not discussed further.

3.4.2 Nickel Cadmium

The nickel cadmium (NiCad) battery was considered to be one of the main competitors to the lead acid battery for use in EVs and these batteries have nearly twice the specific energy of lead acid batteries.

The NiCad battery uses a nickel oxyhydroxide for the positive electrode and metallic cadmium for the negative electrode. Electrical energy is obtained from the following reaction:

 $Cd + 2 NiOOH + 2 H_2O \leftrightarrow Cd(OH)_2 + 2 Ni(OH)_2$



Figure 3.7 Reactions during the discharge of a nickel cadmium cell. The reactions are reversed during charge

The reactions at each electrode, which also helps to explain 'where the electrons come from' and how the battery works, are shown in Figure 3.7. This battery makes an interesting comparison with the lead acid in that here the electrolyte becomes more concentrated as the cell discharges.

NiCad batteries have been widely used in many appliances including use in EVs. The NiCad battery has advantages of high specific power, a long life cycle (up to 2500 cycles), a wide range of operating temperatures from -40 to +80 °C, a low self-discharge and good long-term storage. This is because the battery is a very stable system, with equivalent reactions to the self-discharge of the lead acid battery (Equations 3.4 and 3.5) only taking place very slowly. The NiCad battery can be purchased in a range of sizes and shapes, though they are not easy to obtain in the larger sizes required for EVs, their main market being portable tools and electronic equipment. They are also very robust both mechanically and electrically and can be recharged within an hour and up to 60% capacity in 20 minutes.

On the negative side, the operating voltage of each cell is only about 1.2 V, so 10 cells are needed in each nominally 12 V battery, compared with 6 cells for the lead acid. This partly explains the higher cost of this type of battery. A further problem is that the cost of cadmium is several times that of lead, and this is not likely to change. Cadmium is also environmentally harmful and carcinogenic.

The high cost of a NiCad battery, typically three times that of lead acid ones, is offset to an extent by its longer cycle life. Its charge efficiency decreases rapidly above $35 \,^{\circ}C$ but this is unlikely to affect its use in EVs. It has been used successfully in cars such as electric versions of the Peugeot 106, the Citroen AX and the Renault Clio, as well as the Ford Th!nk car. The overall characteristics of the battery are given in Table 3.2.

As with lead acid batteries, NiCad batteries need to be properly charged. *The points made in* Section 3.8 *below apply to this type of battery as well*. However, because NiCad cells are less prone to self-discharge, the problem raised there is not so great as with lead acid cells. Normally the battery is charged at a constant current until its cell voltages reach a predetermined level, at which point the current is switched off. At this point the cell voltages decay to a lower predetermined voltage and the current is switched back on. This process is continued until the battery is recharged. A good proportion of the charge

Specific energy Energy density Specific power	40-55 Wh kg ⁻¹ depending on current 70-90 Wh1 ⁻¹ depending on current \sim 125 W kg ⁻¹ before becoming very inefficient
Nominal cell voltage	1.2 V
Amphour efficiency	Good
Internal resistance	Very low, $\sim 0.06 \Omega$ per cell for a 1 Ah cell
Commercially available	Good in smaller sizes, difficult for larger batteries
Operating temperature	-40 to $+80 ^{\circ}\text{C}$
Self-discharge	0.5% per day, very low
Number of life cycles	1200 to 80% capacity
Recharge time	1 h, rapid charge to 60% capacity 20 min

 Table 3.2
 Nominal battery parameters for nickel cadmium batteries

can be normally be replaced within 1 hour, but as explained in Section 3.8, the cell must be run at a fairly low current, with most of the cells being overcharged, for a longer time. Alternatively the battery can be recharged at a lower, constant current – this is a simpler system, but takes longer.

A clever feature of the NiCad battery is the way that it copes with overcharging. The cell is made so that there is a surplus of cadmium hydroxide in the negative electrode. This means that the positive electrode will always be fully charged first. A continuation of the charging current results in the generation of oxygen at the positive electrode via the reaction

$$4 \text{ OH}^- \rightarrow 2 \text{ H}_2 \text{ O} + \text{ O}_2 + 4 \text{ e}^-$$
 (3.6)

The resulting free oxygen diffuses to the negative electrode, where it reacts with the cadmium, producing cadmium hydroxide, using the water produced by reaction 3.6:

$$O_2 + 2 \operatorname{Cd} + 2 \operatorname{H}_2 O \to 2 \operatorname{Cd}(OH)_2 \tag{3.7}$$

As well as this reaction, the normal charging reaction will be taking place at this electrode, using the electrodes produced by reaction 3.4:

$$2 \operatorname{Cd}(\operatorname{OH})_2 + 4 \operatorname{e}^- \to 2 \operatorname{Cd} + 4 \operatorname{OH}^-$$
(3.8)

Comparing reactions 3.7 and 3.8 we see that the rate of production of cadmium hydroxide is exactly equal to its rate of conversion back to cadmium. We thus have a perfectly sustainable system, with no net use of any material from the battery. The sum total of the reactions 3.6–3.8 is *no effect*. This overcharging situation can thus continue indefinitely. For most NiCad batteries their size and design allow this to continue for ever at the C_{10} rate, that is at 10 A for a 100 Ah battery. Of course this overcharging current represents a waste of energy, but it is not doing any harm to the battery, and is necessary in some cells while charging the battery in the final phase to equalise all the cells to fully charged.

It should be noted that although the internal resistance of the NiCad battery is very low, it is not as low as for the lead acid battery. This results in a somewhat lower maximum economic specific power. The empirical, good 'first-approximation' formula² for the internal resistance of a NiCad battery is

$$R = \text{no. of cells} \times \frac{0.06}{C_3} \,\Omega \tag{3.9}$$

Comparing this with Equation (3.3) for the lead acid cell, it can be seen that there is a higher number (0.06 instead of 0.022). Also the number of cells will be greater, as has already been explained.

3.4.3 Nickel Metal Hydride Batteries

The NiMH battery was introduced commercially in the last decade of the twentieth century. It has a similar performance to the NiCad battery, the main difference being that in the NiMH battery the negative electrode uses hydrogen, absorbed in a metal hydride, which makes it free from cadmium, a considerable advantage.

An interesting feature of this battery type is that the negative electrode behaves *exactly* like a fuel cell, an energy source we consider more fully in the next chapter.

The reaction at the positive electrode is the same as for the NiCad cell; the nickel oxyhydroxide becomes nickel hydroxide during discharge. At the negative electrode hydrogen is released from the metal to which it was temporarily attached, and reacts, producing water and electrons. The reactions at each electrode are shown in Figure 3.8.

The metals that are used to hold the hydrogen are alloys, whose formulation is usually proprietary. The principle of their operation is exactly the same as in the metal hydride



Figure 3.8 The reactions during the discharge of the nickel metal hydride cell. When charged the reactions are reversed. Note that when both discharging and charging water is created at exactly the same rate at which it is used, and that therefore the electrolyte does not change with state of charge

 $^{^2}$ The factor 0.06 in this formula is based on measurements from a small sample of good-quality NiCad traction batteries.

hydrogen stores used in conjunction with fuel cells, and described in more detail in Chapter 5. The basic principle is a reversible reaction in which hydrogen is bonded to the metal and then released as free hydrogen when required. For this to work the cell must be sealed, as an important driver in the absorption/desorption process is the pressure of the hydrogen gas, which is maintained at a fairly constant value. A further important point about the sealing is that the hydrogen-absorbing alloys will be damaged if air is allowed into the cell. This is because they will react with the air, and other molecules will occupy the sites used to store the hydrogen.

The overall chemical reaction for the NiMH battery is written as

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

In terms of energy density and power density the metal hydride cell is somewhat better than the NiCad battery. NiMH batteries have a nominal specific energy of about 65 Wh kg^{-1} , a nominal energy density of 150 Wh l^{-1} and a maximum specific power of about 200 W kg^{-1} . Table 3.3 gives this and other information about this class of battery. In most respects its performance is similar to, or a little better than, that for the NiCad cell. The nominal cell voltage is 1.2 V.

One area where the NiMH is better than the NiCad is that it is possible to charge the battery somewhat faster. Indeed, it can be charged so fast that cooling becomes necessary. As well as heat energy being created by the normal internal resistance of the battery, the reaction in which hydrogen is bonded to the metal adjacent to the negative electrode is quite strongly exothermic. Unless the vehicle is a cycle or scooter, with a small battery, a cooling system is an important feature of NiMH battery systems. They are available commercially in small sizes, but the larger batteries suitable for EVs are beginning to appear. An example of a commercial NiMH battery is shown in Figure 3.9. Notice that the battery has cooling fans fitted as an integral part of the casing, for the reason explained above.

The NiMH battery has slightly higher energy storage capacity than NiCad systems, and is also a little more costly. There is one area where its performance is notably worse than that for NiCad batteries, and that its self-discharge properties. Hydrogen molecules are very small, and they can reasonably easily diffuse through the electrolyte to the positive

Specific energy	\sim 65 Wh kg ⁻¹ depending on power
Energy density	$\sim 150 \mathrm{Wh} \mathrm{l}^{-1}$
Specific power	$200 \mathrm{W kg^{-1}}$
Nominal cell voltage	1.2 V
Amphour efficiency	Quite good
Internal resistance	Very low, $\sim 0.06 \Omega$ per cell for a 1 Ah cell
Commercially available	A good range of small cells, traction batteries difficult to obtain
Operating temperature	Ambient
Self-discharge	Poor, up to 5% per day
Number of life cycles	~ 1000 to 80% discharge
Recharge time	1 h, rapid charge to 60% capacity 20 min

 Table 3.3
 Nominal battery parameters for nickel metal hydride batteries



Figure 3.9 A commercial NiMH battery, with integral cooling fans

electrode, where it will react:

$$\frac{1}{2}H_2 + \text{NiOOH} \rightarrow \text{Ni(OH)}_2$$

This effectively discharges the cell – hydrogen is lost from the negative electrode and nickel hydroxide is formed at the positive electrode. The result is that this battery is subject to quite rapid self-discharge.

An interesting feature of the cell, which can be seen by reference to Figure 3.8, is that the composition of the electrolyte does not change during charge or discharge – both water and OH^- ions are created and used at exactly the same rate. The result is that the internal resistance and open-circuit voltage of the cell are much more constant during discharge than with either lead acid or NiCad batteries. Being backed by a metal layer, the cell has an internal resistance that is also a little lower – but not greatly different.

The charging regime is similar to the NiCad battery, the current being switched on and off to keep the cell voltage between an upper and a lower limit. Like NiCad batteries, the NiMH battery can be charged within 1 h. Most cells can cope with an overcharge current of about 0.1*C*, like the NiCad cell. As will be explained in Section 3.9, overcharging is necessary in a battery to make sure each and every cell is fully charged.

Of all the new battery systems NiMH is considered to be one of the most advanced and has been used in a range of vehicles including the Toyota Prius. The market volume of NiMH batteries is still small, but with quantity production the price will drop.

3.5 Sodium-Based Batteries

3.5.1 Introduction

From the 1980s a range of batteries which use a liquid sodium negative electrode have been developed. These batteries differ from other batteries inasmuch as they run at high temperatures. They also have the interesting feature of using one or more liquid electrodes in the form of molten sodium and using a solid ceramic electrolyte. Because of the need to operate at high temperatures they are only practical for large systems, such as electric cars – they are not suitable for scooters and cycles. They are rather more exotic than other types, as they will never be used in mobile phones or laptop computers, unlike the other types of battery we will consider in this chapter. This limitation on their market has rather impeded their commercial development.

3.5.2 Sodium Sulfur Batteries

The development of these batteries started in the 1970s and they run at temperatures between 300 and $350 \,^{\circ}$ C. In order to keep the heat in the battery, the cells are enclosed in an evacuated case. The basic sodium sulfur cells have a high specific energy, six times that of lead acid cells, but in experimental batteries the mass of the enclosure typically halves this potential improvement.

The negative electrode in the cells consists of molten sodium, and the positive electrode consists of molten sulfur polysulfides. The electrolyte is a solid beta alumina ceramic, which conducts the sodium ions and also separates the two electrodes. The actual cells are kept fairly small, and they are joined together and placed in an evacuated chamber to cut down heat losses. The design of the container needs careful thought as it can double the mass of the battery. Before the batteries can be used they have to be heated slowly to their working temperature. When in use the cells are essentially self-heating due to the electric current passing through the battery internal resistance. When not in use for more than a day the battery's interior has to be kept hot by the use of electrical heaters. The electrical energy is obtained from combining sodium with sulfur to form sodium sulfide.

The basic chemical formula for the reaction is

$$2 \text{Na} + x\text{S} \leftrightarrow \text{Na}_2\text{S}_x$$

The overall characteristics of the battery are given in Table 3.4.

Specific energy	100 Wh kg^{-1} (potentially 200 Wh kg ⁻¹)
Energy density	150 Wh l ⁻¹
Specific power	$200 \mathrm{W kg^{-1}}$
Nominal cell voltage	2 V
Amphour efficiency	Very good
Internal resistance	Broadly similar to NiCad
Commercially available	Not on the market at all
Operating temperature	300–350 °C
Self-discharge	Quite low, but when not in use energy must be supplied to keep the battery warm
Number of life cycles	~ 1000 to 80% capacity
Recharge time	8 h

 Table 3.4
 Nominal battery parameters for sodium sulfur batteries. As always, the performance figures depend on usage

Because of the need for good thermal insulation small batteries are impractical. The battery heating and cooling needs careful design and management. Although the sodium sulfur battery has considerable promise, worries about the safety of two reactive materials separated by a brittle ceramic tube have largely resulted in the batteries not appearing on the commercial market. These fears were boosted by spontaneous fires involving test vehicles during trials.

3.5.3 Sodium Metal Chloride (ZEBRA) Batteries

The sodium metal chloride or Zebra³ battery is in many ways similar to the sodium sulfur battery and has many of this battery's advantages. However, with this system most (and some would say all) of the safety worries associated with the sodium sulfur battery have been overcome. The principal reason for the greater safety of the Zebra cells is the use of the solid positive electrolyte which is separated from the molten sodium metal by both solid and liquid electrolytes. It is certainly the case that prototype Zebra batteries have passed qualification tests for Europe, including rigorous tests such as crashing the cell at 50 kph into a steel pole (Vincent and Scrosati, 1997, p. 272). This battery has considerable promise and it can be obtained commercially.

The Zebra cell uses solid nickel chloride for the positive electrode and molten sodium for the negative electrode. Two electrodes are used, a beta ceramic electrode surrounding the sodium and a secondary electrolyte, sodium–aluminium chloride, is used in the positive electrode chamber. Chlorine ions are the mobile ion in the electrolyte. The electrical energy on discharge is obtained by combining sodium with nickel chloride to give nickel and sodium chloride. The overall chemical reaction which takes place in the Zebra battery is:

$2 \operatorname{Na} + \operatorname{NiCl}_2 \leftrightarrow \operatorname{Ni} + 2 \operatorname{NaCl}$

Figure 3.10 shows the reactions at each electrode during the middle and early part of the discharge of the cell. This reaction produces an open-circuit voltage of about 2.5 V per cell. In the later stages of the discharge the reactions become more complex, involving aluminium ions from the electrolyte, and resulting in a lower voltage. Indeed an unfortunate feature of this type of cell is the way that the cell voltage falls during discharge, from about 2.5 V down to around 1.6 V. The internal resistance of the cell also increases, further affecting the output voltage. Nevertheless, as can be seen from the data in Table 3.5, the specific energy is very high, even with these effects.

A major problem with the Zebra battery is that it needs to operate at a temperature of about $320 \,^{\circ}$ C, similar to the sodium sulfur battery. Heat insulation is maintained by the use of a double-skinned stainless steel box, with $2-3 \,\mathrm{cm}$ of insulation between the two skins. All the air is removed from the insulation, and the vacuum is maintained for several years. Nevertheless, unless it is for a very short period, a few hours, these batteries need to be kept connected to a mains supply when not in use. This is to keep the battery hot, and is a major limitation to their application. As an example, the battery shown in Figure 3.11, which fits neatly under the seat of a battery electric car, holds an impressive 17.8 kWh

³ ZEBRA is an acronym for the Zero Emissions Battery Research Association. However, it has now rather lost this connection, and is used as a name for this type of battery.



Figure 3.10 The reactions at each electrode of the sodium metal chloride battery during discharge

 Table 3.5
 Nominal battery parameters for sodium metal chloride (Zebra) batteries

Specific energy	$100 \mathrm{Wh} \mathrm{kg}^{-1}$
Energy density	$150 \mathrm{Wh} \mathrm{l}^{-1}$
Specific power	$150 \mathrm{W kg^{-1}}$
Nominal cell voltage	$\sim 2 \text{ V}$ average (2.5 V when fully charged)
Amphour efficiency	Very high
Internal resistance	Very low, but higher at low levels of charge
Commercially available	Available commercially, but very few suppliers
Operating temperature	300–350 °C
Self-discharge	When not in use energy must be continually used to keep the battery up to temperature, corresponding to a self-discharge of about 10% per day
Number of life cycles	>1000
Recharge time	8 h



Figure 3.11 A commercial Zebra battery fitted neatly under the seat of an experimental battery electric vehicle by MES-DEA. The battery stores about 18 kWh of electrical energy

of energy. However, when not in use it consumes about 100 W of power keeping up to temperature. So, in a 24 hour period the heating will require $0.1 \times 24 = 2.4$ kWh of energy, corresponding to about 13% of the stored energy. In energy terms, this corresponds to the self-discharge of other types of battery, and is quite a high figure.

Zebra batteries can be allowed to cool, but if this happens they must be reheated slowly and steadily, a process typically taking about 24 hours. They are available as tried and tested units with well-established performance criteria, though only in a very limited range of size. An example is shown in Figure 3.11.

The overall characteristics of the battery are given in Table 3.5. These are taken from the 17.8 kWh (\sim 280 V, 64 Ah, 180 kg, 32 kW peak power) unit manufactured by MES-DEA of Switzerland.

3.6 Lithium Batteries

3.6.1 Introduction

Since the late 1980s rechargeable lithium cells have started to come on the market. They offer greatly increased energy density in comparison with other rechargeable batteries, though at increased cost although this is coming down. It is a well-established feature of the most expensive laptop computers and mobile phones that lithium rechargeable batteries are specified, rather than the lower cost NiCad or NiMH cells that we considered earlier.

Up until the advent of lithium batteries, the development of suitable batteries for EVs could arguably be viewed as somewhat pedestrian. Battery development has recently leapt forward considerably and lithium batteries have developed to the point where motor manufacturers are prepared to mass-produce EVs. We have not yet reached the stage where commercial lithium batteries are fully developed, but there are predictions that by 2020 lithium batteries will have specific energies greater than 300 Wh kg⁻¹, approximately 10 times that of lead acid batteries.

3.6.2 The Lithium Polymer Battery

The lithium polymer battery uses lithium metal for the negative electrode and a transition metal intercalation oxide for the positive one. In the resulting chemical reaction the lithium combines with the metal oxide to form a lithium metal oxide and release energy. When the battery is recharged the chemical reaction is reversed. The lithium is thus both a reactant and the mobile ion that moves through the electrolyte. The overall chemical reaction is

$$xLi + M_yO_z \leftrightarrow Li_xM_yO_z$$

The solid lithium negative electrode has been a cause of problems with this type of cell, namely safety difficulties and sometimes a decrease in performance due to passivation. Thus these cells have been largely superseded by the lithium ion battery.

3.6.3 The Lithium Ion Battery

Lithium ion batteries are a family of rechargeable types in which lithium ions move from the negative electrode to the positive electrode during discharge, and back when charging. Chemistry, performance, cost and safety characteristics vary across these types.

A lithium ion battery is a rechargeable battery in which lithium ions move between the anode and cathode, creating a flow of electricity. Lithium in the anode (carbon material) is ionised and emitted to the electrolyte. Lithium ions move through a porous plastic separator and into the cathode. At the same time, electrons are released from the anode. This becomes an electric current travelling to an outside electric circuit. During charging, lithium ions go from the cathode to the anode through the separator. Since this is a reversible chemical reaction, the battery can be recharged.

The three primary functional components of a lithium ion battery are the anode, cathode and electrolyte. The anode of a conventional lithium ion cell is made from carbon, the cathode is a metal oxide, and the electrolyte is a lithium salt in an organic solvent.

The most commercially popular anode material is graphite. The cathode 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).

The electrolyte is typically a mixture of organic carbonates. Depending on the choice of materials, the voltage, capacity, life and safety of a lithium ion battery can change dramatically. Recently, novel architectures using nanotechnology have been employed to improve performance.

Pure lithium reacts vigorously with water so that a non-aqueous electrolyte is used, and a sealed container rigidly excludes water from the battery pack.

Lithium ion batteries are more expensive than NiCad batteries but operate over a wider temperature range with higher energy densities, while being smaller and lighter. They are fragile and so need a protective circuit to limit peak voltages.

Initially used for consumer electronics, the lithium ion battery (LIB) is growing in popularity for EV applications. Research is yielding a stream of improvements to traditional LIB technology, focusing on energy density, durability, cost and safety.

The LIB was introduced in the early 1990s and used a lithiated transition metal intercalation oxide for the positive electrode and lithiated carbon for the negative electrode. The electrolyte is either a liquid organic solution or a solid polymer.

Electrical energy is obtained from the combination of the lithium carbon and the lithium metal oxide to form carbon and lithium metal oxide. The overall chemical reaction for the battery is

$$Li_x + M_yO_z \leftrightarrow 6C + Li_xM_yO_z$$

The essential features of the battery are given in Table 3.6. An important point about LIBs is that accurate control of voltage is needed when charging lithium cells. If it is slightly too high it can damage the battery; too low and the battery will be insufficiently charged. Suitable commercial chargers are being developed along with the battery.

The LIB has a considerable weight advantage over other battery systems and this makes it a highly attractive candidate for EVs. The specific energy, for example, is

Specific energy	$140 {\rm Whkg^{-1}}$
Energy density	$250-620 \text{ Wh } 1^{-1}$
Specific power	$300 - 1500 \mathrm{W kg^{-1}}$
Nominal cell voltage	3.5 V
Amphour efficiency	Very good
Internal resistance	Very low
Commercially available	Larger LIBs have become the standard battery for electric road vehicles
Operating temperature	Ambient
Self-discharge	Very low, $\sim 10\%$ per month
Number of life cycles	>1000
Recharge time	$2{-}3h,$ but can be charged to 80% of their capacity in under $1h$

Table 3.6	Nominal	properties	of lithium	ion	batteries
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about three times that of lead acid batteries, and this could give a car a very reasonable range. However, large batteries have until recently been prohibitively expensive, though the price has now dropped to the point where the LIB is the preferred battery for EVs. With recent developments and improved specific energies large companies have set up production lines.

As with most components a ready market combined with quantity production often leads to rapid development and further price reductions. Most modern EVs including the Nissan Leaf, the Mitsubishi MiEV, the Tesla Roadster and the Chevrolet Volt use LIBs. The battery in the Leaf has a capacity of 24 kWh and the specific energy of the cells is 140 Wh kg^{-1} . The predicted development of the battery by 2015 will give a specific energy of 200 Wh kg⁻¹.

3.7 Metal–Air Batteries

3.7.1 Introduction

The metal-air batteries represent an entirely different development, in the sense that the batteries cannot be recharged simply by reversing the current. Instead the spent metal electrodes must be replaced or reprocessed. The metal electrodes can thus be considered as a kind of fuel. The spent fuel is then sent to a reprocessing plant where it will be turned into new 'fuel'. The battery electrolyte will also normally need to be replaced.

This is not a dissimilar concept to conventional IC engine vehicles where they stop periodically to refuel, with the added advantage that the vehicle will have the main attributes of an EV – quietness and zero emissions. As such it may appeal to motorists who are used to refuelling their vehicles and may be slow to adapt to change.

3.7.2 The Aluminium–Air Battery

The basic chemical reaction of the aluminium-air battery is essentially simple. Aluminium is combined with oxygen from the air and water to form aluminium hydroxide,

Specific energy	$225 \mathrm{Whkg}^{-1}$
Energy density	195 Wh 1 ⁻¹
Specific power	$10 \mathrm{W kg^{-1}}$
Nominal cell voltage	1.4 V
Amphour efficiency	n/a
Internal resistance	Rather high, hence low power
Commercially available	Stationary systems only available
Operating temperature	Ambient
Self-discharge	Very high (>10% per day) normally, but the electrolyte can be pumped out, which makes it very low
Number of life cycles	1000 or more
Recharge time	10 min, while the fuel is replaced

 Table 3.7
 Nominal battery parameters for aluminium-air batteries

releasing electrical energy in the process. The reaction is irreversible. The overall chemical reaction is

$$4 \text{Al} + 3 \text{O}_2 + 6 \text{H}_2\text{O} \rightarrow 4 \text{Al}(\text{OH})_3$$

The aluminium forms the negative electrode of the cell, and it typically starts as a plate about 1 cm thick. As the reaction proceeds the electrode becomes smaller and smaller. The positive electrode is typically a porous structure, consisting of a metal mesh onto which is pressed a layer of catalysed carbon. A thin layer of polytetrafluoroethylene (PTFE) gives it the necessary porosity to let the oxygen in but prevent the liquid electrolyte getting out. The electrolyte is an alkaline solution, usually potassium hydroxide.

The battery is recharged by replacing the used negative electrodes. The electrolyte will normally also be replenished, as it will be contaminated with the aluminium hydroxide.

The essential characteristics of the aluminium–air battery are listed in Table 3.7. The big drawback of the aluminium–air battery is its extremely low specific power. For example, a 100 kg battery would give only 1000 W, which is clearly insufficient to power a road vehicle. To get a power output of 20 kW, 2 tonnes of battery would be needed. The battery, on its own, is therefore not likely to be useful for most road vehicles.

3.7.3 The Zinc–Air Battery

The zinc-air battery is similar in many ways to the aluminium-air battery but has a much better overall performance – particularly with regard to specific power, which is nearly 10 times that of the aluminium-air battery, making it suitable for use in road vehicles. The structure is similar, with a porous positive electrode at which oxygen reacts with the electrolyte. The electrolyte is a liquid alkaline solution. The negative electrode is solid zinc.

The energy from the battery is obtained by combining zinc with the oxygen in the air and forming zinc oxide. Alternatively, depending on the state of the electrodes and electrolyte, zinc hydroxide may be formed, as for the aluminium–air cell. The process is normally irreversible.

Specific energy	$230 \mathrm{Wh}\mathrm{kg}^{-1}$
Energy density	$270 \mathrm{Wh}\mathrm{l}^{-1}$
Specific power	$105 \mathrm{W kg^{-1}}$
Nominal cell voltage	1.2 V
Amphour efficiency	Not applicable
Internal resistance	Medium
Commercially available	Very few suppliers
Operating temperature	Ambient
Self-discharge	High as electrolyte is left in cell
Number of life cycles	>2000
Recharge time	10 min, while the fuel is replaced

 Table 3.8
 Nominal battery parameters for zinc-air batteries

The general characteristics of the battery are given in Table 3.8. A few manufacturers have claimed to produce electrically rechargeable zinc-air batteries, but the number of cycles is usually quite small. The more normal way of recharging is as for the aluminium-air cell, which is by replacing the negative electrodes. The electrolyte, containing the zinc oxide, is also replaced. In principle this could be taken back to a central plant and the zinc recovered, but the infrastructure for doing this would be rather inconvenient.

Small zinc-air batteries have been available for many years, and their very high energy density makes them useful in applications such as hearing aids. These devices are usually 'on' virtually all the time, and thus the self-discharge is not so much of a problem. Large batteries, with replaceable negative electrodes, are only available with great difficulty, but this is changing, and they show considerable potential for the future. Use of a replaceable fuel has considerable advantages as it avoids the use of recharging points – lorries delivering fuel can simply take the spent fuel back to the reprocessing plant from where they got it in the first place. The high specific energy will also allow reasonable journey times between stops.

3.8 Supercapacitors and Flywheels

3.8.1 Supercapacitors

Supercapacitors or ultracapacitors are large capacitors which can be used as energy stores. They are devices which have high specific power and low specific energy.

Capacitors are devices with two conducting plates which are separated by an insulator. An example is shown in Figure 3.12. A DC voltage is connected across the capacitor, one plate being positive, the other negative. The opposite charges on the plates attract and hence store energy. The charge Q stored in a capacitor of capacitance C farads at a voltage of V volts is given by the equation

$$Q = C \times V \tag{3.10}$$

As with flywheels, capacitors can provide large energy storage, although they are more normally used in small sizes as components in electronic circuits. The large energy storing



Opposite charges on plates attract each other, thus storing energy

Figure 3.12 Principle of the capacitor

capacitors with large plate areas have come to be called 'supercapacitors'. The energy stored in a capacitor is given by the equation

$$E = \frac{1}{2}CV^2 \tag{3.11}$$

where E is the energy stored in joules. The capacitance C of a capacitor in farads will be given by the equation

$$C = \varepsilon \frac{A}{d} \tag{3.12}$$

where ε is the permittivity of the material between the plates, A is the plate area and d is the separation of the plates. The key to modern supercapacitors is that the separation of the plates is so small. The capacitance arises from the formation on the electrode surface of a layer of electrolytic ions (the 'double layer'). They have high surface areas, for example 1 000 000 m² kg⁻¹, and a 4000 F capacitor can be fitted into a container the size of a beer can.

However, the problem with this technology is that the voltage across the capacitor can only be very low, between 1 and 3 V. The problem with this is clear from Equation (3.11): it severely limits the energy that can be stored. In order to store charge at a reasonable voltage many capacitors have to be connected in series. This not only adds costs, but brings other problems too.

If two capacitors C_1 and C_2 are connected in series then it is well known⁴ that the combined capacitance C is given by the formula

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \tag{3.13}$$

⁴ Along with all the equations in this section, a full explanation or proof can be found in any basic electrical circuits or physics textbook.

So, for example, two 3 F capacitor in series will have a combined capacitance of 1.5 F. Putting capacitors in series *reduces* the capacitance. Now, the energy stored increases as the voltage *squared*, so it does result in more energy stored, but not as much as might be hoped from a simple consideration of Equation (3.13).

Another major problem with putting capacitors in series is that of charge equalisation. In a string of capacitors in series the charge on each one should be the same, as the same current flows through the series circuit. However, the problem is that there will be a certain amount of self-discharge in each one, due to the fact that the insulation between the plates of the capacitors will not be perfect. Obviously, this self-discharge will not be equal in all the capacitors – life is not like that! The problem then is that there may be a relative charge build-up on some of the capacitors, and this will result in a higher voltage on those capacitors. It is certain that unless something is done about this, the voltage on some of the capacitors will exceed the maximum of 3 V, irrevocably damaging the capacitor.

This problem of voltage difference will also be exacerbated by the fact that the capacitance of the capacitors will vary slightly, and this will affect the voltage. From Equation (3.10) we can see that capacitors with the same charge and different capacitances will have different voltages.

The only solution to this, and it is essential in systems of more than about six capacitors in series, is to have *charge equalisation circuits*. These are circuits connected to each pair of capacitors that continually monitor the voltage across adjacent capacitors, and move charge from one to the other in order to make sure that the voltage across both capacitors is the same.

These charge equalisation circuits add to the cost and size of a capacitor energy storage system. They also consume some energy, though designs are available that are very efficient and have a current consumption of only 1 mA or so.

A Ragone plot comparing supercapacitors and a flywheel with batteries is shown in Figure 3.13. A supercapacitor energy storage system is shown in Figure 3.14.

In many ways the characteristics of supercapacitors have similarities with flywheels. They have relatively high specific power and relatively low specific energy. They can be used as the energy storage for regenerative braking. While they could be used on a vehicle by themselves they would be better used in a hybrid as devices for giving out and receiving energy rapidly during braking and accelerating afterwards, for example at traffic lights. Supercapacitors are inherently safer than flywheels as they avoid the problems of mechanical breakdown and gyroscopic effects. Power electronics are needed to step voltages up and down as required. Several interesting vehicles have been built with supercapacitors providing significant energy storage, and descriptions of these can be found in the literature. Furubayashi *et al.* (2001) describe a system where capacitors are used with a diesel IC engine. Lott and Späth (2001) describe a capacitors are used with a fuel cell.

3.8.2 Flywheels

Flywheels are devices that are used for storing energy. A plane disc spinning about its axis would be an example of a simple flywheel. The kinetic energy of the spinning disc



Figure 3.13 Ragone plot of batteries, supercapacitors and flywheels



Figure 3.14 A bank of supercapacitors, together with charge equalisation circuits. This is the system that was used in a hybrid diesel electric bus with electrical energy stoted in capacitors (Photograph kindly supplied by MAN Nutzfahrzeuge AG)



Figure 3.15 Principle of flywheel used as an energy store

is released when the flywheel slows down. The energy can be captured by connecting an electrical generator directly to the disc as shown in Figure 3.15, power electronics being required to match the generator output to a form where it can drive the vehicle motors. The flywheel can be reaccelerated, acting as a regenerative brake. Alternatively the flywheel can be connected to the vehicle wheels via a gearbox and a clutch. This transmission matches the rotational speed of the flywheel to the wheels, the flywheel giving out energy as it decelerates.

Whether mechanical or electrical, the system can also be used to recover kinetic energy when braking. The flywheel can be accelerated, turning the kinetic energy of the vehicle into stored kinetic energy in the flywheel, and acting as a highly efficient regenerative brake.

The total amount of energy stored is given by the formula

$$E = 0.5I\omega^2 \tag{3.14}$$

where E is the energy in joules, I is the moment of inertia and ω is the rotational speed in radians per second. When a flywheel reduces from ω_1 to ω_2 radians per second the energy released will be given by the formula

$$\Delta E = 0.5I(\omega_1^2 - \omega_2^2) \tag{3.15}$$

If one could make a flywheel strong enough, almost infinite energy could be stored, bearing in mind that the mass and hence the moment of inertia get larger as the flywheel's peripheral speed approaches the speed of light. Unfortunately, as the flywheel's rotational speed increases so do the stresses in the material. As a result the flywheel's energy storage capacity is limited by the tensile strength of the material it is made from.

The main advantage of flywheels is that they have a high specific power and it is relatively easy to get energy to and from the flywheel. They are also fairly simple, reliable mechanical devices. The specific energy from flywheels is limited and unlikely to approach that of even lead acid batteries. Attempts have been made to boost specific energy by using ultra-strong materials, running the flywheel in an inert gas or a vacuum to reduce air friction losses and using magnetic bearings.

Apart from the low specific energy, there are major worries about safety due to the risk of explosion. In the event of the flywheel rupturing, during a crash, energy is released almost instantly and the flywheel effectively acts like a bomb. Also, if a fast-moving flywheel becomes detached from its mountings it could cause real havoc. Another aspect of flywheels that needs to be considered is the gyroscopic effect of a disc rotating at high speeds. Firstly, without outside interference flywheels tend to stay in one position and do not readily move on an axis other than the axis of spin. When a torque or movement is introduced around one axis, the flywheel tends to move or precess around another axis. Again the behaviour in an accident situation needs studying carefully, as does the effect on the vehicle's dynamics. However, it should be noted that in many cases these effects could be benign, and they could have a smoothing effect on vehicle ride.

Several attempts have been made to produce flywheel buses and trams, the Parry People Mover, we believe, being the only one available commercially. The workings were shown in Figure 2.7. Despite the lack of success of the flywheel for vehicle energy storage and a certain amount of bad press, it would be wrong to write off the flywheel completely. Virtually all IC engines have small flywheels and these have not proved particularly problematic. The simplicity of a small flywheel to be used in an EV for use as a regenerative braking system should not be overlooked. Provided the flywheel is used well below its rupture point and is kept relatively small and well guarded, it may come to have a useful role in the future of EVs, particularly in hybrids.

3.9 Battery Charging

3.9.1 Battery Chargers

The issue of charging batteries is of the utmost importance for maintaining batteries in good order and preventing premature failure. We have already seen, for example, how leaving a lead acid battery in a low state of charge can cause permanent damage through the process of sulfation. However, charging batteries improperly can also very easily damage them.

Charging a modern vehicle battery is not a simple matter of providing a constant voltage or current through the battery, but requires very careful control of current and voltage. The best approach for the designer is to buy commercial charging equipment from the battery manufacturer or other reputed battery charger manufacturer. If the vehicle is to be charged in different places where the correct charging equipment is not available, the option of a modern, light onboard charger should be considered.

Except in the case of photoelectric panels, the energy for recharging a battery will nearly always come from an alternating current (AC) source such as the mains. This will need to be rectified to direct current (DC) for charging the battery. The rectified direct current must have very little ripple – it must be very well 'smoothed'. This is because, at the times when the variation of the DC voltage goes below the battery voltage, no charging will take place, and at the 'high point' of the ripple it is possible that the voltage could be high

enough to damage the battery. The higher the direct current, the harder it is for rectifiers to produce a smooth DC output, which means that the rectifying and smoothing circuits of battery chargers are often quite expensive, especially for high-current chargers. For example, the battery charger for the important development vehicle, the General Motors EV1, cost about \$2000 in 1996 (Shnayerson, 1996).

One important issue relating to battery chargers is the provision of facilities for charging vehicles in public places such as car parks. Some cities in Europe, especially (for example) La Rochelle in France, and several in California in the USA, provide such units. A major problem is that of standardisation, making sure that all EVs can safely connect to all such units. The Californian Air Resources Board (CARB), which regulates such matters there, has produced guidelines, which are described elsewhere (Sweigert, Eley and Childers, 2001). This paper also gives a good outline of the different ways in which these car-to-charger connections can be made.

However, the great majority of EVs, such as bicycles, mobility aids, delivery vehicles and the like, will always use one charger, which will be designed specifically for the battery on that vehicle. On hybrid EVs too, the charger is the alternator on the engine, and the charging will be controlled by the vehicle's energy management system. However, whatever charging method is used, with whatever type of battery, the importance of 'charge equalisation' in batteries must be understood. This is explained in the section following.

3.9.2 Charge Equalisation

An important point that applies to all battery types relates to the process of 'charge equalisation' that *must* be done in all batteries at regular intervals if serious damage is not to result.

A problem with all batteries is that when current is drawn not all the individual cells in the battery lose the same amount of charge. Since a battery is a collection of cells connected in series, this may at first seem wrong – after all, exactly the same current flows through them all. However, it does not occur because of different currents (the electric current is indeed the same) – it occurs because the *self-discharge effects* we have noted (e.g. Equations (3.4) and (3.5) in the case of lead acid batteries) take place at different rates in different cells. This is because of manufacturing variations, and also because of changes in temperature – all the cells in a battery will not be at exactly the same temperature.

The result is that if nominally 50% of the charge is taken from a battery, then some cells will have lost only a little more than this, say 52%, while some may have lost considerably more, say 60%. If the battery is recharged with enough for the good cell, then the cells more prone to self-discharge will not be fully recharged. The effect of doing this repeatedly is shown in Table 3.9.

Cell A cycles between about 20 and 80% charged, which is perfectly satisfactory. However, cell B sinks lower and lower, and eventually fails after a fairly small number of cycles.⁵ If one cell in a battery goes completely flat like this, the battery voltage will fall sharply, because the cell is just a resistance lowering the voltage. If current is still

⁵ The very large difference in self-discharge of this example is somewhat unlikely. Nevertheless, the example illustrates what happens, though usually more slowly than the four cycles of Table 3.9.

State of charge of cell A (%)	State of charge of cell B	Event	
100	100%	Fully charged	
48	40%	50% discharge	
98	90%	50% charge replaced	
35	19%	60% discharge	
85	69%	50% partial recharge	
33	9%	50% discharge	
83	59%	50% partial recharge	
18	Cannot supply it, battery flat!	60% discharge required to get home	

 Table 3.9
 Showing the state of charge of two different cells in a battery

Cell A is a good-quality cell, with low self-discharge. Cell B has a higher self-discharge, perhaps because of slight manufacturing faults, perhaps because it is warmer. The cells are discharged and charged a number of times.

drawn from the battery, that cell is almost certain to be severely damaged, as the effect of driving current through it when flat is to try and charge it the 'wrong way'. Because a battery is a series circuit, one damaged cell ruins the whole battery. *This effect is probably the major cause of premature battery failure*.

The way to prevent this is to charge the battery fully till *each and every* cell is fully charged – a process known as 'charge equalisation' – at regular intervals. This will inevitably mean that some of the cells will run for perhaps several hours being overcharged. Once the majority of the cells have been charged up, current must continue to be put into the battery so that those cells that are more prone to self-discharge get fully charged up.

This is why it is important that a cell can cope with being overcharged. However, as we have seen in Sections 3.3 and 3.4, only a limited current is possible at overcharge – typically about C_{10} . For this reason the final process of bringing all the cells up to fully charged cannot be done quickly. This explains why it takes so much longer to charge a battery fully than to take it to nearly full. The last bit has to be done slowly. It also explains something of the complexity of a good battery charger, and why the battery charging process is usually considerably less than 100% charge efficient. Figure 3.16 shows this process, using an example not quite as extreme as the data in Table 3.9. Unlike Table 3.9 the battery in Figure 3.16 is 'saved' by ensuring that charge equalisation takes place before any cells become completely exhausted of charge.

So far we have taken the process of 'charge equalisation' to be 'equalising all the calls to full'. However, in theory it is possible to equalise the charge in all cells of the battery at any point in the process, by moving charge from one cell to the other – from the more charged to the less charged. This is practical in the case of the supercapacitors considered in the next chapter; however, it is not usually practical with batteries. The main reason is the difficulty of sensing the state of charge of a cell, whereas for a capacitor it is much easier, as the voltage is directly proportional to charge. However, in the case of lithium-based batteries charge equalisation by adding circuits to the battery system is more practical, and is used. Chou *et al.* (2001) give a good description of such a battery management system.



Figure 3.16 Diagram showing the need for periodic charge equalisation in a battery. The upper line (A) shows the state of charge of a normal cell working satisfactorily. The lower line (B) is for a cell more prone to self-discharge. Charge equalisation involves overcharging some of the cells while the others are brought up to full charge. This is occurring in the final 12 time units

This issue of some cells slowly becoming more deeply discharged than others is very important in battery care. There are two particular cases where it is especially important:

- 1. **Opportunistic charging:** Some users are able to put a small amount of charge back into a battery, for example when parked in a location by a charger for a short time. This is helpful, but the user *must* make certain that fairly frequently a full, long charge is given to the battery to bring all cells up to 100% charged.
- 2. **Hybrid electric vehicles:** In these it is desirable to have the battery *not* fully charged normally, so that it can always absorb energy from regenerative braking. However, this must be done with caution, and the battery management system *must* periodically run the battery to fully charged to equalise all the cells to 100% charged.

These issues of battery charging mentioned here apply to all battery types. However, they are more important for cells with higher self-discharge rates – such as the lead acid battery. The only batteries where this is not of the utmost importance is for the small single cells used in electronic products – however, they are not relevant here.

3.10 The Designer's Choice of Battery

3.10.1 Introduction

At a first glance the designer's choice of battery may seem rather overwhelming. In practice it is not that complicated, although choosing the correct size of battery may be. Firstly the designer needs to decide whether he/she is designing a vehicle which will use batteries which are currently available either commercially, or by arrangement with battery manufacturers for prototype use. Alternatively the designer may be designing a futuristic vehicle for a client or as an exercise, possibly as part of an undergraduate course. The designer will also need to decide on the specification and essential requirements of the vehicle. Is the vehicle, for example, being designed for speed, range, capital cost, running costs, overall costs, style, good handling, good aerodynamics, environmental friendliness, and so on, or is the designer looking for an optimum design taking many of these parameters into consideration? Also, is the designer considering a hybrid or non-hybrid vehicle?

3.10.2 Batteries which are Currently Available Commercially

Of the batteries discussed in this chapter, the ones which are available commercially now for use in EVs include: lead acid, NiCad, NiMH, sodium metal chloride (Zebra) and lithium ion. For comparative purposes these batteries are given in Table 3.10.

For a long-term study, there is no substitute for making a mathematical model of the vehicle using information supplied later in the book and comparing the results using different batteries. However, for some vehicles the choice of battery is fairly obvious and the mathematical model can simply be used to confirm vehicle size and overall performance.

For example, lead acid is cheap and for uses not requiring large amounts of energy storage; for example, for short-range vehicles such as golf carts and wheelchairs, which can be charged overnight, there is no better choice of battery. Lead acid is widely used, has a long track record and has the lowest cost per kilowatt-hour of storage capacity.

Battery	Specific energy $(Wh kg^{-1})$	Energy density (Wh l ⁻¹)	Specific power (W kg ⁻¹)	Current cost
Lead acid	30	75	250	0.5
NiCad	50	80	150	1.5
NiMH	65	150	200	2.0
Zebra	100	150	150	2.0
Li ion	150	150	300	3.0
Zinc-air	230	270	105	?

 Table 3.10
 Comparison of commercially available batteries

The cost figure is an arbitrary unit for broad comparative purposes; all the other figures are also very much guidelines only. We have explained that all such performance figures depend on how the battery is used.

NiMH is a good choice where range and performance are needed. It also can be recharged very quickly, and for uses where the vehicle can be charged frequently this could result in a smaller and cheaper battery unit than, for instance, if a lead acid battery were used. It would therefore come into its own for hybrid vehicles or vehicles such as a commuter bus or tram that stopped frequently and could therefore be charged when stopped.

Sodium metal chloride (Zebra) batteries are not used in small sizes because the heat losses are proportionally large. The Zebra battery has many of the attributes of NiMH, but with even greater energy density. However, the fact that it needs to be kept hot is a major drawback to its use in IC engine/electric hybrids, as these are largely totally autonomous vehicles which may be left unused for long periods – for example, in an airport car park during a two week holiday.

Lithium ion has a good specific energy, energy density and specific power and where performance is required has become one of the main choices for electric road cars.

3.11 Use of Batteries in Hybrid Vehicles

3.11.1 Introduction

There are many combinations of batteries, engines and mechanical flywheels which all allow optimisation of EVs. The best known is the combination of IC engine and rechargeable battery, but more than one type of battery can be used in combination and use of batteries and flywheels can have advantages.

3.11.2 IC/Battery Electric Hybrids

Where IC engine efficiency is to be optimised by charging and supplying energy from the battery, clearly a battery which can be rapidly charged is desirable. This tends to emphasise batteries such as the NiMH which is efficient and readily charged and discharged. An example of this would be in the Toyota Prius and the Honda Insight, both very successful hybrids that use NiMH batteries although on recent versions LIBs will be used. A zinc-air battery would be no use in this situation, as it cannot be electrically recharged.

This type of hybrid electric vehicle – an IC engine with a battery that cannot be recharged from the mains – was until recently the most common. It seems that the majority of such vehicles currently use NiMH batteries, with a storage capacity typically between about 2 and 5 kWh. (Note that the energy stored in a normal car battery is between about 0.3 and 1.0 kWh.) The very latest hybrids, such as the mains rechargeable Chevrolet Volt, use LIBs.

3.11.3 Battery/Battery Electric Hybrids

Different batteries have different characteristics and they can sometimes be combined to give optimum results. For example, an aluminium–air battery has a low specific power and cannot be recharged, but could be used in combination with a battery which recharges and discharges quickly and efficiently – such as the NiMH battery. The aluminium–air battery could provide a base load supplying surplus electricity to the NiMH battery when

the power was not required. The energy from the NiMH battery could then be supplied for accelerating in traffic or overtaking; it could also be used for accepting and resupplying electricity for regenerative braking.

3.11.4 Combinations using Flywheels

Flywheels driving a vehicle through a suitable gearbox can be engineered to store small amounts of energy quickly and efficiently and resupply it soon afterwards. They can be used with mechanisms such as a cone/ball gearbox. They could be usefully employed with batteries that could not do this. For example, the zinc–air battery cannot be recharged in its location on the vehicle, and hence cannot be used for regenerative braking, but by combining this with a suitable flywheel a vehicle using a zinc–air battery with regenerative braking could be designed.

3.11.5 Complex Hybrids

There is plenty of scope for originality from designers. Two or more batteries, an IC engine and a flywheel, for example, may achieve the optimum combination. Alternatively a fuel cell could be combined with a battery and a flywheel.

3.12 Battery Modelling

3.12.1 The Purpose of Battery Modelling

Modelling (or simulating) of engineering systems is always important and useful. It is done for different reasons. Sometimes models are constructed to understand the effect of changing the way something is made. For example, we could construct a battery model that would allow us to predict the effect of changing the thickness of the lead oxide layer of the negative electrodes of a sealed lead acid battery. Such models make extensive use of fundamental physics and chemistry, and the power of modern computers allows the models to be made with very good predictive powers.

Other types of models are constructed to predict accurately the behaviour of a particular make and model of battery in different circumstances. This model will then be used to predict the performance of a vehicle fitted with that type of battery. This sort of model relies more on careful analysis of real performance data than fundamental physics and chemistry.

In this book we will concern ourselves only with the latter type of performance modelling. However, all modelling of batteries is notoriously difficult and unreliable. The performance of a battery depends on reasonably easily measurable quantities such as its temperature, and performance characteristics such as voltage. However, it also depends on parameters far harder to specify precisely, such as age and the way the battery has been used (or misused) in the past. Manufacturing tolerances and variations between the different cells within a battery can also have a big impact on performance.

The result of these problems is that all we can do here is give an introduction to the task of battery simulation and modelling.

3.12.2 Battery Equivalent Circuit

The first task in simulating the performance of a battery is to construct an 'equivalent circuit'. This is a circuit made up of elements, and each element has precisely predictable behaviour.

We introduced such an equivalent circuit at the beginning of this chapter. Figure 3.1 is a very simple (but still highly useful) equivalent circuit for a battery. A limitation of this type of circuit is that it does not explain the dynamic behaviour of the battery at all. For example, if a load is connected to the battery the voltage will immediately change to a new (lower) value. In fact this is not true; rather the voltage takes time to settle down to a new value.

Figure 3.17 shows a somewhat more refined equivalent circuit that simulates or models these dynamic effects quite well. We could carry on refining our circuit more and more to give an ever-closer prediction of performance. These issues are discussed in the literature, for example by Johnson, Zolot and Pesaran (2001).

The purpose of our battery simulations is to be able to predict the performance of EVs, in terms of range, acceleration, speed, and so on -a topic covered in reasonable depth in Chapter 8. In these simulations the speed of the vehicles changes fairly slowly, and the dynamic behaviour of the battery makes a difference that is small compared with the other approximations we have to make along the way. Therefore, in this introduction to battery simulation we will use the basic equivalent circuit of Figure 3.1.

Although the equivalent circuit of Figure 3.1 is simple, we do need to understand that the values of the circuit parameters (E and R) are not constant. The open-circuit voltage of the battery E is the most important to establish first. This changes with the state of charge of the battery.

In the case of the sealed lead acid battery we have already seen that the open-circuit voltage E is approximately proportional to the state of charge of the battery, as in Figure 3.6. This shows the voltage of one cell of a battery. If we propose a battery variable DoD, meaning the depth of discharge of a battery, which is 0 when fully charged and 1.0 when empty, then the simple formula for the open-circuit voltage is

$$E = n \times [2.15 - DoD \times (2.15 - 2.00)]$$
(3.16)



Figure 3.17 Example of a more refined equivalent circuit model of a battery. This models some of the dynamic behaviour of a battery

where n is the number of cells in the battery. This formula gives reasonably good results for this type of battery, though a first improvement would be to include a term for the temperature, because this has a strong impact.

In the case of nickel-based batteries such a simple formula cannot be constructed. The voltage/state of charge curve is far from linear. Fortunately it now very easy to use mathematical software, such as MATLAB[®], to find polynomial equations that give a very good fit to the results. One such, produced from experimental results from a NiCad traction battery, is

$$E = n \times (-8.2816 \, DoD^7 + 23.5749 \, DoD^6 - 30 \, DoD^5 + 23.7053 \, DoD^4 - 12.5877 \, DoD^3 + 4.1315 \, DoD^2 - 0.8658 \, DoD + 1.37)$$
(3.17)

The purpose of being able to simulate battery behaviour is to use the results to predict vehicle performance. In other words, we wish to use the result in a larger simulation. This is best done in software such as MATLAB[®] or a Microsoft Excel spreadsheet. Which program is used depends on many factors, including issues such as what the user is used to. For the purposes of a book like this, MATLAB[®] is the most appropriate, since it is very widely used, and it is much easier than Excel to explain what you have done and how to do it.

A useful feature of MATLAB[®] is the ability to create functions. Calculating the value of *E* is a very good example of where such a function should be used. The MATLAB[®] function for finding *E* for a lead acid battery is as follows:

```
function E_oc=open_circuit_voltage_LA(x,N)
% Find the open-circuit voltage of a lead acid
% battery at any value of depth of discharge.
% The depth of discharge value must be between
% 0 (fully charged) and 1.0 (flat).
if x<0
        error('Depth of discharge <0.');
end
if x > 1
error('Depth of discharge >1')
end
% See equation (3.16) in text.
E_oc= (2.15 - ((2.15-2.00)*x)) * N;
```

The similar function for a NiCad battery is identical, except that the last line is replaced by a formula corresponding to Equation (3.17).

Our very simple battery model of Figure 3.1 now has a means of finding E, at least for some battery types. The internal resistance also needs to be found. The value of R is approximately constant for a battery, but it is affected by the state of charge and by temperature. It is also increased by misuse – and this is especially true of lead acid batteries. Simple first-order approximations for the internal resistance of lead acid and nickel-based batteries have been given in Equations (3.2) and (3.9).

3.12.3 Modelling Battery Capacity

We have seen in Section 3.2.2 that the capacity of a battery is reduced if the current is drawn more quickly. Drawing 1 A for 10 h does *not* take the same charge from a battery as running it at 10 A for 1 h.

This phenomenon is particularly important for EVs, as in this application the currents are generally higher, with the result that the capacity might be less than expected. It is important to be able to predict the effect of current on capacity, both when designing vehicles and when making instruments that measure the charge left in a battery – battery fuel gauge. Knowing the depth of discharge of a battery is also essential for finding the open-circuit voltage using Equations (3.16) and (3.17).

The best way to do this is to use the Peukert model of battery behaviour. While not very accurate at low currents, for higher currents it models battery behaviour well enough.

The starting point of this model is that there is a capacity, called the Peukert capacity, which is constant and is given by the equation

$$C_p = I^k T \tag{3.18}$$

where k is a constant (typically about 1.2 for a lead acid battery) called the Peukert coefficient. This equation assumes that the battery is discharged till flat, at a constant current I amps, and that this will last T hours. Note that the Peukert capacity is equivalent to the normal amphours capacity for a battery discharged at 1 A. In practice the Peukert capacity is calculated as in the following example.

Suppose a battery has a nominal capacity of 40 Ah at the 5 h rate. This means that it has a capacity of 40 Ah if discharged at a current of:

$$I = \frac{40}{5} = 8 \,\mathrm{A} \tag{3.19}$$

If the Peukert coefficient is 1.2, then the Peukert capacity is

$$C_p = 8^{1.2} \times 5 = 60.6 \,\mathrm{Ah} \tag{3.20}$$

We can now use Equation (3.18) (rearranged) to find the time that the battery will last at *any* current I:

$$T = \frac{C_p}{I^k} \tag{3.21}$$

The accuracy of this Peukert model can be seen by considering the battery data shown in Figure 3.2. This is for a nominally 42 Ah battery (10 h rate) and shows how the capacity changes with discharge time. The solid line in Figure 3.18 shows the data of Figure 3.2 in a different form; that is, it shows how the capacity declines with increasing discharge current. Using methods described below, the Peukert coefficient for this battery has been found to be 1.107. From Equation (3.18) we have

$$C_p = 4.2^{1.107} \times 10 = 49 \,\mathrm{Ah}$$

Using this, and Equation (3.15), we can calculate the capacity that the Peukert equation would give us for a range of currents. This has been done with the crosses in Figure 3.18. As can be seen, these are quite close to the graph of the measured, real, values.



Figure 3.18 Showing how closely the Peukert model fits real battery data. In this case the data is from a nominally 42 V lead acid battery

The conclusion from Equations (3.18) and (3.21) is that if a current I flows from a battery, then, from the point of view of the battery capacity, the current that *appears* to flow out of the battery is I^k amps. Clearly, as long as I and k are greater than 1.0 then I^k will be larger than I.

We can use this in a real battery simulation and see we how the voltage changes as the battery is discharged. This is done by doing a step-by-step simulation, calculating the charge removed at each step. This can be done quite well in Excel, but for reasons explained earlier, MATLAB[®] will be used here.

The time step between calculations we will call δt . If the current flowing is *I* amps, then the apparent or effective charge removed from the battery is

Loss of charge =
$$\delta t \times I^k$$
 (3.22)

There is a problem of units here. If δt is in seconds, this will be have to be divided by 3600 to bring the units into amphours. If CR_n is the total charge *removed* from the battery by the *n*th step of the simulation, then we can say that

$$CR_{n+1} = CR_n + \frac{\delta t \times I^k}{3600} \text{ Ah}$$
(3.23)

It is very important to keep in mind that this is the charge removed from the plates of the battery. It is *not* the total charge actually supplied by the battery to the vehicle's electrics.

This figure, which we could call CS, charge supplied, is given by the formula

$$CS_{n+1} = CS_n + \frac{\delta t \times I}{3600} \text{ Ah}$$
(3.24)

This formula will normally give a *lower* figure. As we saw in the earlier sections, this difference is caused by self-discharge reactions taking place *within* the battery.

The depth of discharge of a battery is the ratio of the charge removed to the original capacity. So, at the nth step of a step-by-step simulation we can say that

$$DOD_n = \frac{CR_n}{C_p} \tag{3.25}$$

Here C_p is the Peukert capacity, as from Equation (3.18). This value of depth of discharge can be used to find the open-circuit voltage, which can then lead to the actual terminal voltage from the simple equation already given as Equation (3.1).

To simulate the discharge of a battery these equations are 'run through', with n going from 1, 2, 3, 4, and so on, until the battery is discharged. This is reached when the depth of discharge is equal to 1.0, though it is more common to stop just before this, say when DoD = 0.99.

The script file below runs one such simulation for a NiCad battery.

```
% Simple battery constant current discharge experiment for
% a large 5 cell NiCad battery. The time step is set to 50
% seconds, which is sufficiently small for such a constant
% current experiment.
% We need to form some arrays for holding data. The array T
% is for time, which will run from 0 to 50000 seconds, in
% 50 second steps.
T = (0:50:50000);
% This corresponds to 1001 values. We form four more arrays,
% each also with 1001 elements, and all with initial values
% of zero. Dod(n) is used to store values of the depth of
% discharge, V(n) stores voltage values, CR(n) and CS(n)
% store values of the charge, in amphours, removed from the
% battery and supplied by the battery.
CR=zeros(1,1001); % Charge removed from electrodes,
% corrected using Peukert coefficient.
DoD=zeros(1,1001); % Depth of discharge, start off fully
% charged.
V=zeros(1,1001); % Battery voltage at each time step
CS=zeros(1,1001); % Charge supplied by the battery in Ah
% We now set some constants for the experiment.
I = 30; % Set discharge current to 30 amps
NoCells=5; % 5 cell battery
Capacity=50; % This is the normal 3h rated capacity of the
                             % battery
k=1.045;
                  % Peukert coefficient, not much greater than 1.
```

```
deltaT = 50;
                 % Take 10 second time steps, OK for con I.
% Calculated values
Rin= (0.06/Capacity) *NoCells; % Internal resistance, e.g. (3.9)
PeuCap= ((Capacity/3)^k)*3;
                             % See equation (3.18)
% Starting voltage set outside loop
V(1) = open_circuit_voltage_NC(0, NoCells) - I*Rin; % Equation (3.1)
for n=2:1001
CR(n) = CR(n-1) + ((1^k * deltaT)/3600);  Equation (3.23)
DoD(n) = CR(n)/PeuCap; % Equation (3.25)
if DoD(n) > 1
DoD(n) = 1:
end
V(n)=open_circuit_voltage_NC(DoD(n),NoCells) - I*Rin;
% We will say that the battery is "dead" if the
% depth of discharge exceeds 99%.
if DoD(n)>0.99
V(n) = 0;
end
% We now calculate the real amphours given out by the
% battery. This uses the actual current, NOT Peukert
% corrected.
if V(n) > 0
CS(n) = CS(n-1) + ((I*deltaT)/3600);  Equation (3.24)
else
CS(n) = CS(n-1);
end
end
%The battery V could be plotted against t, but it is sometimes
% more useful to plot against Ah given out. This we do here.
plot(CS,V,'b.');
axis([0 55 3.5 7]);
XLABEL('Charge supplied/Amphours');
YLABEL('Battery voltage/Volts');
TITLE('Constant current discharge of a 50Ah NiCad battery');
```

This script file runs the simulation at one unchanging current. Figures 3.19 and 3.20 show the graphs of voltage for three different currents. The voltage is plotted against the actual CS by the battery, as in Equation (3.24). The power of this type of simulation can be seen by comparing Figure 3.15 with Figure 3.16, which is a copy of the similar data taken from measurements of the real battery.

3.12.4 Simulating a Battery at a Set Power

When making a vehicle go at a certain speed, then it is a certain *power* that will be required from the motor. This will then require a certain electrical power from the battery. It is thus useful to be able to simulate the operation of a battery at a certain set power, rather than current.



Figure 3.19 Showing the voltage of a 6 V NiCad traction battery as it discharges for three different currents. These are simulated results using the model described in the text



Figure 3.20 Results similar to those of Figure 3.19, but these are measurements from a real battery (By kind permission of SAFT)

The first step is to find an equation for the current I from a battery when it is operating at a power P watts. In general we know that

$$P = V \times I$$

If we then combine this with the basic equation for the terminal voltage of a battery, which we have written as Equation (3.1), we get

$$P = V \times I = (E - IR) \times I = EI - RI^2$$

This is a quadratic equation for I. The normal useful solution⁶ to this equation is

$$I = \frac{E - \sqrt{E^2 - 4RP}}{2R} \tag{3.26}$$

This equation allows us easily to use MATLAB[®] or similar mathematical software to simulate the constant power discharge of a battery. The MATLAB[®] script file below shows this done for a lead acid battery. The graph of voltage against time is shown in Figure 3.21.



Figure 3.21 Graph of voltage against time for a constant power discharge of a lead acid battery at 5000 W. The nominal ratings of the battery are 120 V, 50 Ah

⁶ As with all quadratics, there are two solutions. The other corresponds to a 'lunatic' way of operating the battery at a huge current, so large that the internal resistance causes the voltage to drop to a low value, so that the power is achieved with a low voltage and very high current. This is immensely inefficient.

```
% A constant P discharge experiment for a lead acid battery.
% The system has 10 batteries, each 12V lead acid, 50Ah.
% We use 10 s steps, as these are sufficiently small for
% a constant power discharge. We set up arrays to store the
% data.
T=(0:10:10000); % Time goes up to 10,000 in 10 s steps.
                                     % This is 1001 values.
CR=zeros(1,1001); % Charge rem. from bat. Peukert corrected.
DoD=zeros(1,1001); % Depth of discharge, start fully charged.
V=zeros(1,1001); % Battery voltage, initially set to zero.
NoCells=60; % 10 of 6 cell (12 V) batteries.
Capacity=50; % 50 Ah batteries, 10h rate capacity.
                         % Peukert coefficient
k=1.12;
deltaT = 10; % Take 10 s steps, OK for constant power.
P = 5000; % We will drain the battery at 5 kW.
% Calculated values
Rin= (0.022/Capacity)*NoCells;
                                   % Internal res., Equation (3.2)
PeuCap= ((Capacity/10)^k)*10; % See Equation (3.18)
% Starting voltage set outside loop
E=open_circuit_voltage_LA(0,NoCells);
I = (E - (E*E - (4*Rin*P))^{0.5})/(2*Rin);
                                             %Equation (3.26)
V(1) = E - I*Rin;
                                     %Equation (3.1)
for n=2:1001
E=open_circuit_voltage_LA(DoD(n-1), NoCells); %Equation (3.16)
I = (E - (E*E - (4*Rin*P))^{0.5})/(2*Rin); %Equation (3.26)
CR(n) = CR(n-1) + ((deltaT * I^k)/3600);
                                              %Equation (3.23)
DoD(n) = CR(n) / PeuCap;
                                              %Equation (3.25)
if DoD(n) > 1
DoD(n) = 1;
end
% We will say that the battery is "dead" if the
% depth of discharge exceeds 99%.
V(n)=open_circuit_voltage_LA(DoD(n),NoCells) - I*Rin; %Equation (3.1)
if DoD(n)>0.99
V(n) = 0;
end
end
plot(T,V,'b.');
YLABEL('Battery voltage/Volts');
XLABEL('Time/Seconds');
TITLE('Constant power discharge of a lead acid battery');
axis([0 4000 100 140]);
```

When we come to simulate the battery being used in a vehicle, the issue of regenerative braking will arise. Here a certain power is dissipated *into* the battery. If we look again at Figure 3.1, and consider the situation if the current I is flowing *into* the battery, then the equation becomes

$$V = E + IR \tag{3.27}$$

If we combine this equation with the normal equation for power we obtain

$$P = V \times I = (E + IR) \times I = EI + RI^2$$

The 'sensible', normal efficient operation, solution to this quadratic equation is

$$I = \frac{-E + \sqrt{E^2 + 4RP}}{2R}$$
(3.28)

The value of R, the internal resistance of the cell, will normally be different when charging as opposed to discharging. To use a value twice the size of the discharge value is a good first approximation.

When running the simulation, we must remember that the power P is positive and that Equation (3.28) gives the current *into* the battery. So when incorporating regenerative braking into battery simulation, care must be taken to use the right equation for the current, and that Equation (3.23) must be modified so that the charge *removed* from the battery is *reduced*. Also, it is important to remove the Peukert correction, as when charging a battery large currents do not have proportionately more effect than small ones. Equation (3.23) thus becomes

$$CR_{n+1} = CR_n - \frac{\delta t \times I}{3600} \operatorname{Ah}$$
(3.29)

We meet this equation again in Section 8.4.2, where we simulate the range and performance of EVs with and without regenerative braking.

3.12.5 Calculating the Peukert Coefficient

These equations and simulations are very important and will be used again when we model the performance of EVs in Chapter 8. There the powers and currents will not be constant, as they were above, but exactly the same equations are used.

However, all this begs the question 'How do we find out what the Peukert coefficient is?' It is very rarely given on a battery specification sheet, but fortunately there is nearly always sufficient information to calculate the value. All that is required is the battery capacity at *two different discharge times*. For example, the nominally 42 Ah (10 h rating) of Figure 3.2 also has a capacity of 33.6 Ah at a 1 h rating.

The method of finding the Peukert coefficient from 2 Ah ratings is as follows. The two different ratings give two different rated currents

$$I_1 = \frac{C_1}{T_1}$$
 and $I_2 = \frac{C_2}{T_2}$ (3.30)

We then have two equations for the Peukert capacity, as in Equation (3.12):

$$C_p = I_1^k \times T_1 \quad \text{and} \quad C_p = I_2^k \times T_2 \tag{3.31}$$

However, since the Peukert coefficient is constant, the right hand sides of both parts of Equation (3.31) are equal, and thus

$$I_1^k T_1 = I_2^k T_2$$

and so

$$\left(\frac{I_1}{I_2}\right)^k = \frac{T_2}{T_1}$$

Taking logs, and rearranging, this gives

$$k = \frac{(\log T_2 - \log T_1)}{(\log I_1 - \log I_2)}$$
(3.32)

This equation allows us to calculate the Peukert coefficient k for a battery, provided we have two values for the capacity at two different discharge times T. Taking the example of our 42 Ah nominal battery, Equation (3.30) becomes

$$I_1 = \frac{C_1}{T_1} = \frac{42}{10} = 4.2 \text{ A} \text{ and } I_2 = \frac{C_2}{T_2} = \frac{33.6}{1} = 33.6 \text{ A}$$

Putting these values into Equation (3.32) gives

$$k = \frac{\log 1 - \log 10}{\log 4.2 - \log 33.6} = 1.107$$

Such calculations can be done with any battery, provided some quantitative indication is given as to how the capacity changes with rate of discharge. If a large number of measurements of capacity at different discharge times are available, then it is best to plot a graph of $\log(T)$ against $\log(I)$. Clearly, from Equation (3.32), the gradient of the best-fit line of this graph is the Peukert coefficient.

As a general rule, the lower the Peukert coefficient, the better the battery. All battery types behave in a similar way and are quite well modelled using this method. The Peukert coefficient tends to be rather higher for lead acid batteries than for other types.

3.12.6 Approximate Battery Sizing

The modelling techniques described above, when used with the models for vehicles described in Chapter 8, should be used to give an indication of the performance that will be obtained from a vehicle with a certain type of battery. However, it is possible, and sometimes useful, to get a very approximate guide to battery range and/or size using the approach outlined below.

A designer may be either creating a new vehicle or alternatively adapting an existing vehicle to an electric car. The energy consumption of an existing vehicle will probably be known, in which case the energy used per kilometre can be multiplied by the range and divided by the specific energy of the battery to give an approximate battery mass.

If the vehicle is a new design the energy requirements may be obtained by comparing it with a vehicle of similar design. Should the similar vehicle have an IC engine, the energy consumption can be derived from the fuel consumption and the engine/gearbox efficiency.

This method is fairly crude, but none the less may give a reasonable answer which can be analysed later.

For example, the vehicle may be compared with a diesel engine car with a fuel consumption of 18 km l^{-1} (~50 mpg). The specific energy of diesel fuel is approximately 40 k Wh kg^{-1} and the conversion efficiency of the engine and transmission is approximately 10%, resulting in 4 kWh of energy per litre of fuel stored delivered at the wheels.

In order to travel 180 km the vehicle will consume 101 of fuel, approximately 11 kg allowing for fuel density. This fuel has an energy value of 440 kWh, and the energy delivered to the wheels will be 44 kWh ($44\,000 \text{ Wh}$) allowing for the 10% efficiency. This can be divided by the electric motor and transmission efficiency, typically about 0.7 (70%), to give the energy needed from the battery, that is 62.8 kWh or 62 800 Wh.

Hence if a lead acid battery is used (specific energy 35 Wh kg^{-1}) the battery mass will be 1257 kg, if an NiMH battery (specific energy 60 Wh kg^{-1}) is used the battery mass will be 733 kg, if a sodium nickel chloride battery is used of a specific energy of 86 Wh kg^{-1} then the battery mass will be 511 kg, and if a zinc-air battery of 230 Wh kg⁻¹ is used then a battery mass of 191 kg is needed.

Care must be taken when using specific energy figures, particularly, for example when a battery such as a lead acid battery is being discharged rapidly when the specific energy actually obtained will be considerably lower than the nominal 35 Wh kg⁻¹. However, this technique is useful, and in the case quoted above gives a fairly good indication of which batteries would be ideal, which would suffice and which would be ridiculously heavy. The technique would also give a 'ballpark figure' of battery mass for more advanced analysis, using the modelling techniques introduced above, and much further developed in Chapter 8.

3.13 In Conclusion

There have been massive improvements in batteries in recent years, and several new developments are showing considerable promise. Nevertheless the specific energies of batteries are still relatively low but these are improving all the time. For the first time lithium batteries have developed sufficiently to allow motor manufacturers to mass-produce and sell battery EVs.

It can be concluded that:

- Lead acid batteries are only really suited for short-range vehicles. They remain the cheapest form of battery per unit of energy stored and it is likely that they will continue to be widely used for these purposes. Very many useful EVs can be made which do not need a long range.
- 2. Some of the newer batteries such as lithium have sufficient energy density to be used for medium-range vehicles and can be charged relatively rapidly, which makes them ideal for use in hybrid cars, with range extenders, or for a vehicle such as a bus or tram, which can be recharged during frequent stops. Provided that predicted price decreases continue to be realised, these batteries are likely to be increasingly used.
- 3. There are no batteries that currently show signs of enabling pure EVs to compete for both versatility and long-range use with IC engines, although EVs use batteries which have sufficient range for over 90% of all journeys. Hybrid vehicles have much longer ranges while using electricity from rechargeable batteries for most of their journeys.

4. Predicted future batteries may have considerably enhanced specific energies. A report in *The Economist* (6 March 2008) predicts that new lithium technology will enable batteries to have specific energies of $350 \text{ Wh} \text{kg}^{-1}$ as early as 2020. This will give a battery 2.5 times the specific energy of the current battery such as that used in the Nissan Leaf. It is very important to monitor constantly developments in batteries as well as their cost.

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