Module 9: Energy Storage

Lecture 31: Batteries

Batteries

Introduction

A battery consists of two or more electric cells joined together. The cells convert chemical energy to electrical energy. The cells consist of positive and negative electrodes joined by 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 most well known rechargeable type, but there are others. The first electric vehicle using rechargeable batteries preceded the invention of the rechargeable lead acid by 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, lithium polymer and lithium iron, sodium sulphur and sodium metal chloride.

In this lecture the different types of the energy storage devices are presented. The following topics are covered in this lecture:

- Overview of Batteries
- Battery Parameters
- Lead acid batteries
- Lithium ion batteries
- Metal air batteries
- Battery Charging

Overview of Batteries

From the electric vehicle designer's point of view the battery can be treated as a 'black box' which has a range of performance criteria. These criteria will include:

- specific energy
- energy density
- specific power
- typical voltages
- amp hour efficiency
- energy efficiency
- commercial availability
- cost, operating temperatures
- self-discharge rates
- number of life cycles
- recharge rates

The designer also needs to understand how energy availability varies with regard to:

- ambient temperature
- charge and discharge rates
- battery geometry
- optimum temperature
- charging methods
- cooling needs.

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.

Battery Parameters

- ***Cell and battery voltages***

All electric cells have nominal voltages which gives the approximate voltage when the cell is delivering electrical power. The cells can be connected in series to give the overall voltage required. The 'internal resistance' and the equivalent circuit of a battery is shown in **Figure 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 Fig. 1, then by basic circuit theory we can say that:

$$V = E - IR \tag{1}$$

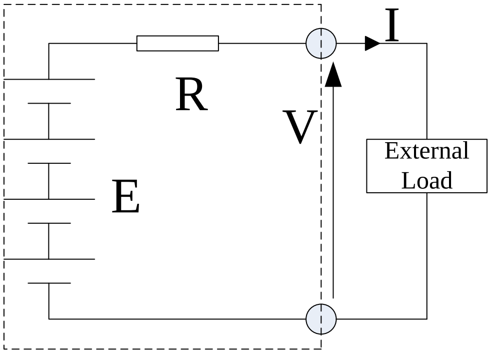


Fig. 1 Simple equivalent circuit model of a battery. This battery is composed of six cells

- ***Charge (or Ahr) 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 one Amp flows for one second. The capacity of a battery might be, say, 10Amphours. This means it can provide 1Amp for 10 hours.

- ***Energy stored***

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 Whr instead.

$$Energy\ in\ Whr = V \times Ahr \tag{2}$$

- ***Specific energy***

Specific energy is the amount of electrical energy stored for every kilogram of battery mass. It has units of $Wh.kg^{-1}$.

- ***Energy density***

Energy density is the amount of electrical energy stored per cubic metre of battery volume. It normally has units of $Wh.m^{-3}$.

- ***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.

- ***Ahr (or charge) efficiency***

In an ideal world a battery would return the entire charge put into it, in which case the amp hour efficiency is 100%. However, no battery does; its 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.

- ***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.

- ***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 rate varies with battery type, and with other factors such as temperature; higher temperatures greatly increase self-discharge.

- ***Battery temperature, heating and cooling needs***

Although 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, but 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.

- ***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 in the lifetime of the battery, which in turn reflects in electric vehicle running costs.

Lead Acid Batteries

- ***Introduction***

The best known and most widely used battery for electric vehicles is the lead acid battery. Lead acid batteries are widely used in IC engine vehicles and as such are well known. However for electric vehicles, 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, whilst the positive plates have an active material of lead dioxide. The plates are immersed in an electrolyte of dilute sulphuric acid. The sulphuric acid combines with the lead and the lead oxide to produce lead sulphate and water, electrical energy being released during the process. The overall reaction is:

$$Pb + PbO_2 + 2H_2SO_4 \leftrightarrow 2PbSO_4 + 2H_2O \qquad (3)$$

The reactions on each electrode of the battery are shown in Fig. 2. In the upper part of the diagram the battery is discharging. Both electrode reactions result in the formation of lead sulphate. The electrolyte gradually loses the sulphuric acid, and becomes more dilute.

When being charged, as in the lower half of **Figure 2**, the electrodes revert to lead and lead dioxide. The electrolyte also recovers its sulphuric acid, and the concentration rises.

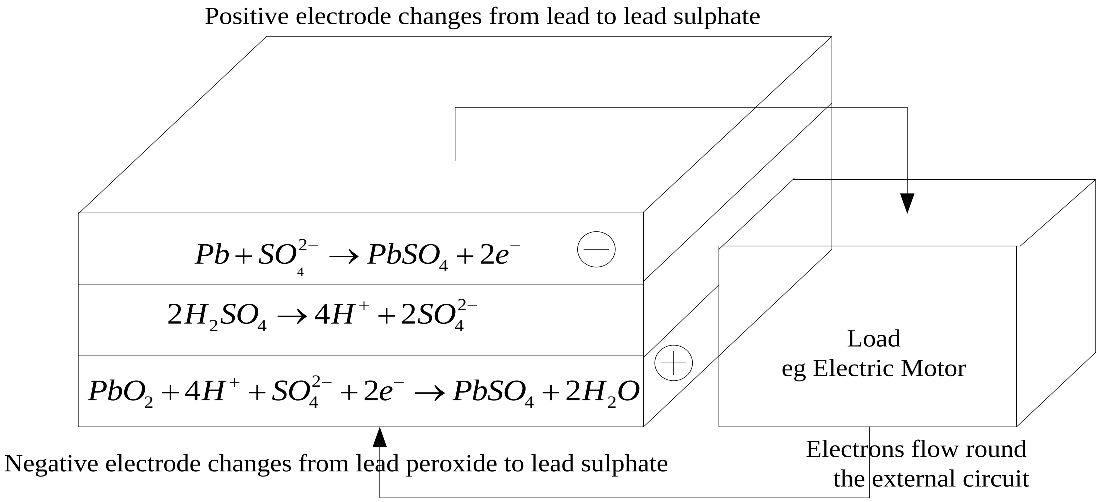
The lead acid battery is the most commonly used rechargeable battery in anything but the smallest of systems. The main reasons for this are that the main constituents (lead, sulphuric acid, a plastic container) are not expensive, that it performs reliably, and that it has a comparatively high voltage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

The figure given in **Table I** of 0.022 Ω per cell is a rule of thumb figure taken from a range of good quality traction batteries. A good estimate of the internal resistance of a lead acid battery is thus:

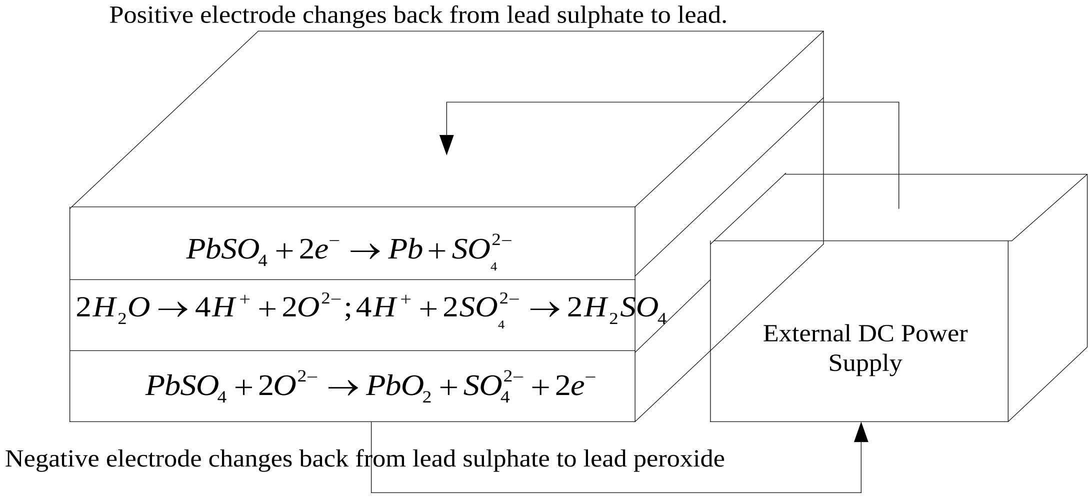
$$R = No.\ of\ \ Cells \times \frac{0.022}{C_{10}} Ohms \tag{4}$$

Table I Nominal battery parameters for lead acid batteries

Specific energy	20–35 Wh.kg−1 depending on usage
Energy density	54–95Wh.L−1
Specific power	~250 W.kg−1 before efficiency falls very greatly
Nominal cell voltage	2V
Amphour efficiency	~80%, varies with rate of discharge & temp.
Internal resistance	Extremely low, ~0.022_ per cell for 1 Amphour cell
Commercially available	Readily available from several manufacturers
Operating temperature	Ambient, poor performance in extreme cold
Self-discharge	~2% per day, but see text below
Number of life cycles	Up to 800 to 80% capacity
Recharge time	8 h (but 90% recharge in 1 h possible)



Reactions during the discharge of the lead acid battery.
Note that the electrolyte loses suphuric acid and gains water.



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

Fig. 2 The reactions during the charge and discharge of the lead acid battery

- ***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.

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 steps 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 the current is then switched on again.

Lithium Batteries

Since the late 1980s rechargeable lithium cells have come onto the market. They offer greatly increased energy density in comparison with other rechargeable batteries, though at greatly increased cost. 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 NiHM cells that we have been considering earlier.

The lithium batteries are of following types:

- Lithium polymer batteries
- Lithium ion batteries

In the following subsections each of the above two battery types are described.

The lithium polymer battery

The lithium polymer battery uses lithium metal for the negative electrode and a transition metal intercalation oxide for the positive. 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:

$$xLi + M_yO_z \leftrightarrow Li_xM_yO_z \qquad (5)$$

The lithium ion battery

The lithium ion battery was introduced in the early 1990s and it uses 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:

$$C_6Li_x + M_yO_z \leftrightarrow 6C + Li_xM_yO_z \qquad (6)$$

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

Table II Nominal battery parameters for lithium ion batteries.

Specific energy	90 Wh.kg−1
Energy density	153 Wh.L−1
Specific power	300 W.kg−1
Nominal cell voltage	3.5V
Amphour efficiency	Very good
Internal resistance	Very low
Commercially available	Only in very small cells not suitable for electric vehicles
Operating temperature	Ambient
Self-discharge	Very low, ∼10% per month
Number of life cycles	>1000
Recharge time	2–3 h

Metal Air Batteries

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 by new ones. 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.

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

$$4AI + 3O_2 + 6H_2O \rightarrow 4AI(OH)_3 \qquad (7)$$

The aluminium forms the negative electrode of the cell, and it typically starts as a plate about 1cm 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 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 shown in Table III. The big drawback of the aluminium air battery is its extremely low specific power.

Table III Nominal battery parameters for aluminium air batteries

Specific energy	225 Wh.kg−1
Energy density	195 Wh.L−1
Specific power	10 W.kg−1
Nominal cell voltage	1.4V
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	10min, while the fuel is replaced

The zinc air battery

The zinc air battery is similar in many ways to the aluminium air battery but it has a much better overall performance, particularly with regard to specific power which is nearly ten 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. The general characteristics of the battery are shown in Table IV. 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.

Table IV Nominal battery parameters for zinc air batteries

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

Lecture 32: Mathematical Modeling for Lead acid battery

Mathematical Modeling for Lead acid battery

In this lecture the mathematical modeling for energy storage devices are presented. The following topics are covered in this lecture:

- Battery Charging
- The Designer's Choice of Battery
- Use of Batteries in Hybrid Vehicles
- Battery Modeling

Battery Charging

The battery charging involves:

- A battery charger
- Charge equalization

Battery chargers

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 another reputed battery charger manufacturer.

When the vehicle is to be charged in different places where 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 DC 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 DC 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.

Charge equalization

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 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; the cells in a battery will not all 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, says 60%. If the battery is recharged with enough for the good cell, then the cells more prone to self-discharge will not be fully re-charged. The effect of doing this repeatedly is shown in **Table I**.

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. 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 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.*

Table I 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

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

The way to prevent this is to fully charge the battery till each and every cell is fully charged (a process known as charge equalization) 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.

The Designer's Choice of Battery

- ***Introduction***

At first glance the designer's choice of battery may seem a rather overwhelming decision. 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 that 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. For example, designing the vehicle for speed, range, capital cost, running costs, overall costs, style, good handling, good aerodynamics, environmentally friendliness, etc.

Use of Batteries in Hybrid Vehicles

Introduction

There are many combinations of batteries, engines and mechanical flywheels which allow optimization of electric vehicles. 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 the use of batteries and flywheels can have advantages.

Internal combustion/battery electric hybrids

IC engine efficiency is to be optimized by charging and supplying energy from the battery, clearly a battery which can be rapidly charged is desirable. This tends to emphasize batteries such as the nickel metal hydride, which is efficient and readily charged and discharged.

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 nickel metal hydride battery. The aluminium air battery could supply a base load that sends surplus electricity to the NiMH battery when the power is 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.

Combinations using flywheels

Flywheels that drive 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 can be usefully employed with batteries that could not do this. For example the zinc air battery cannot be recharged in location in 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.

Battery Modeling

The purpose of battery modeling

Modeling (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 such models to be made with very good predictive powers.

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 behavior. The equivalent circuit is shown in **Figure 1**. A limitation of this type of circuit is that it does not explain the dynamic behavior 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.

In these simulations the speed of the vehicles changes fairly slowly, and the dynamic behavior of the battery makes a difference that is small compared to 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 1**.

Although the equivalent circuit of **Figure 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.

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. This shows the voltage of one cell of a battery. If we propose a battery variable *DoD (depth-of-discharge)*, meaning the depth of discharge of a battery, which is zero when fully charged and 1.0 when empty, then the simple formula for the open circuit voltage is:

$$E = n \times (2.15 - DoD \times (2.15 - 2.00)) \tag{1}$$

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.

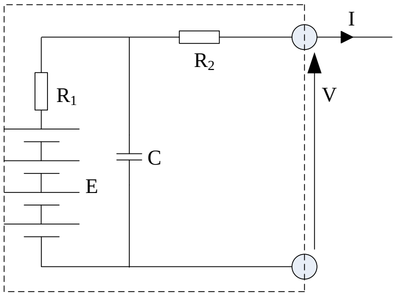


Fig. 1 Example of a more refined equivalent circuit model of a battery. This models some of the dynamic behavior of a battery

$$V = E - IR \tag{2}$$

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 gives a very good fit to the results. One such, produced from experimental results from a NiCad traction battery is:

$$E = n \times \begin{pmatrix} -8.2816DOD^7 + 23.5749DoD^6 - 30DoD^5 + 23.7053DoD^4 \\ -12.5877DoD^3 + 4.1315DoD^2 - 0.8658DoD + 1.37 \end{pmatrix} \tag{3}$$

The purpose of being able to simulate battery behavior 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 an EXCEL spreadsheet.

The simple battery model of **Figure 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.

Modeling battery capacity

The capacity (10Ahr) of a battery is reduced if the current is drawn more quickly. Drawing 1A for 10 hours does not take the same charge from a battery as running it at 10A for 1 hour. This phenomenon is particularly important for electric vehicles, as in this application the currents are generally higher, with the result that the capacity might be less than is 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 gauges.

The best way to do this is using the Peukert model of battery behavior. Although not very accurate at low currents, for higher currents it models battery behavior 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:

$$C_p = I^k T \tag{4}$$

where k is a constant (typically about 1.2 for a lead acid battery) called the Peukert Coefficient. 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:

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

If the Peukert Coefficient is 1.2, then the Peukert Capacity is:

$$C_p = 8^{1.2} \times 5 = 60.6Ah \tag{6}$$

We can now use **equation 4** (rearranged) to find the time that the battery will last at any current *I*.

$$T = \frac{C_p}{I^k} \tag{7}$$

This is for a nominally 42 Ah battery (10 h rate), and shows how the capacity changes with discharge time. This solid line in **Figure 2** shows the data of **Figure 1** in a different form, i.e. 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 6** we have:

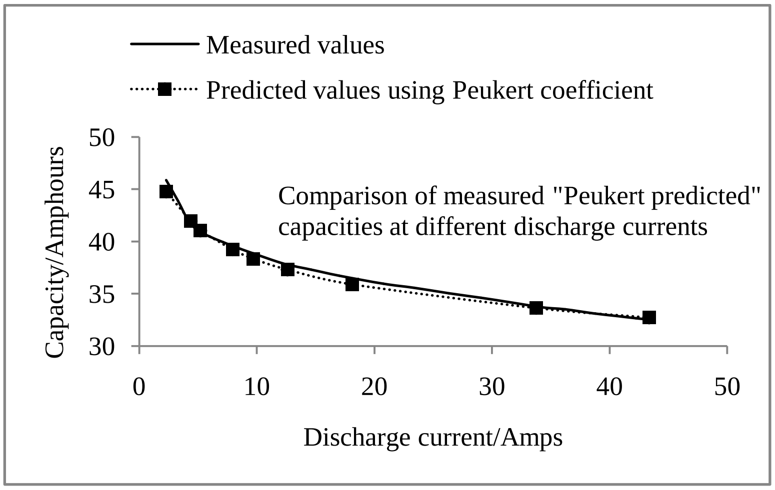


Fig. 2 Showing how closely the Peukert model fits real battery data. In this case the data is from a nominally 42V lead acid Battery

$$C_p = 4.2^{1.107} \times 10 = 49Ahr \tag{8}$$

Using this, and **equation 8**, 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 2**. As can be seen, these are quite close to the graph of the measured real values.

The conclusion from **equation 4** 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 A. 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 we see how the voltage changes as the battery are 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 or MATLAB.

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

$$\delta t \times I^{k} \tag{9}$$

If δt is in seconds, this will be have to be divided by 3600 to bring the units into Amp hours. If CR_n is the total charge removed from the battery by the nth step of the simulation, then we can say that:

$$CR_{n+1} = CR_n + \frac{\delta t \times I^{k}}{3600} Ahr \tag{10}$$

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:

$$CS_{n+1} = CS_n + \frac{\delta t \times I}{3600} Ahr \tag{11}$$

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:

$$DoD_n = \frac{CR_n}{C_p} \tag{12}$$

Where, C_p is the Peukert Capacity, as from **equation 11**. 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 1**. To simulate the discharge of a battery these equations are 'run through', with n going from 1, 2, 3, 4, etc., 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 is 0.99.

Figure 3 shows the graphs of voltage for three different currents. The voltage is plotted against the actual charge supplied by the battery, as in **equation 1**. The power of this type of simulation can be seen by comparing **Figure 3**with Fig. 4, which is a copy of the similar data taken from measurements of the real battery.

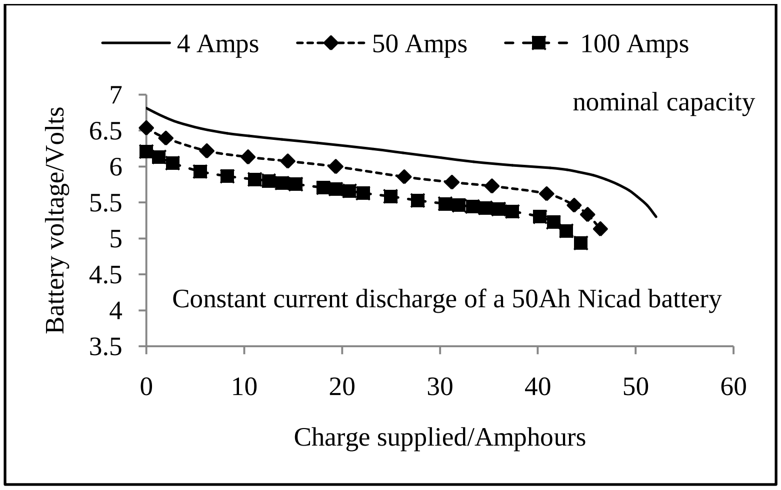


Fig. 3 Showing the voltage of a 6V NiCad traction battery as it discharges for three different currents. These are simulated results using the model described in the text

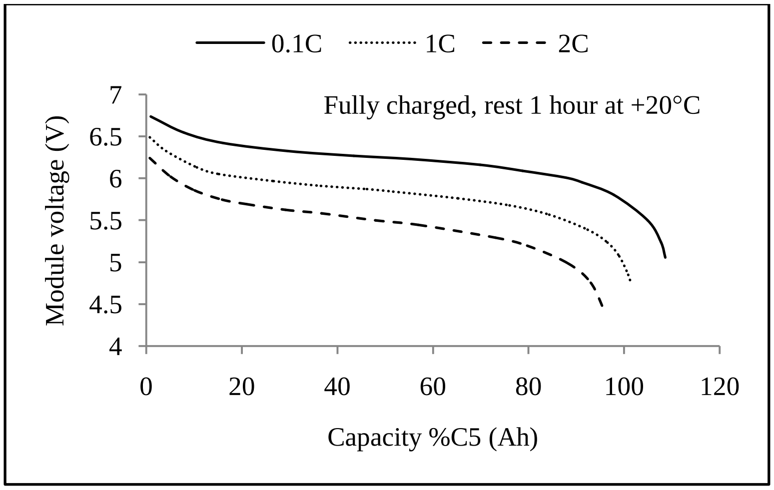


Fig. 4 Results similar to those of Figure m, but these are measurements from a real battery.

- ***Simulation a battery at a set power***

When making a vehicle goes 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. 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:

$$P = V \times I \tag{13}$$

If we then combine this with the basic equation for the terminal voltage of a battery, which we have written as **equation 1**, we get:

$$P = V \times I = (E - IR) \times I = EI - RI^2 \tag{14}$$

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

$$I = \frac{\left(E - \sqrt{E^2 - 4RP}\right)}{2R} \tag{15}$$

This equation allows us to easily use MATLAB or similar mathematical software to simulate the constant power discharge of a battery. The graph of voltage against time is shown in Fig. 5. 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 Fig. 5, and consider the situation that the current *I* is flowing into the battery, then the equation becomes:

$$V = E + IR \tag{16}$$

If we combine **equation 16** with the normal equation for power we obtain:

$$P = V \times I = (E + IR) \times I = EI + RI^2 \tag{17}$$

The ‘sensible’, normal efficient operation, solution to this quadratic equation is:

$$I = \frac{-E + \sqrt{E^2 + 4RP}}{2R} \tag{18}$$

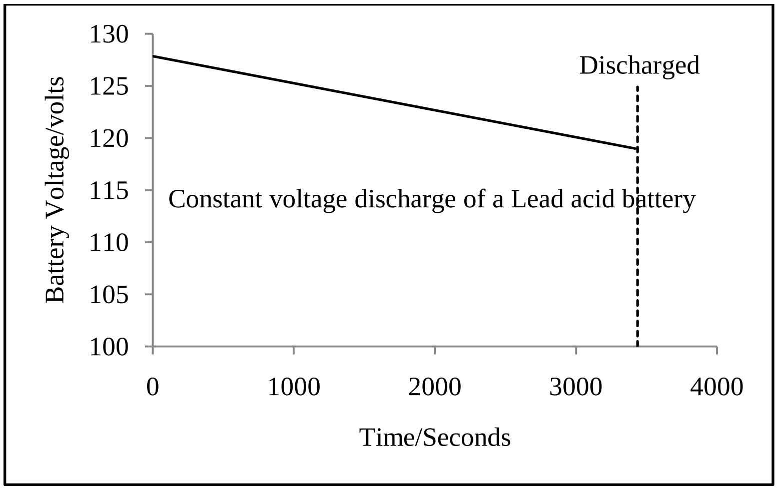


Fig. 5 Graph of voltage against time for a constant power discharge of a lead acid battery at 5000 W. The nominal ratings of the battery are 120 V, 50 Ah

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 a simulation, we must remember that the power *P* is positive, and that Eq. 18 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 Eq. 18 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. Eq. 17 thus becomes:

$$CR_{n+1} = CR_n + \frac{\delta t \times I^k}{3600} Ahr \tag{19}$$

- ***Calculating the Peukert Coefficient***

These equations and simulations are very important, and will be used again when we model the performance of electric vehicles. 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 Coefficien. 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 Ahr (10 hour rating) battery of Fig. 1 also has a capacity of 33.6 Ahr at the 1 hour rate. The method of finding the Peukert Coefficient from two Ahr ratings is as follows. The two different ratings give two different rated currents:

$$I_1 = \frac{C_1}{T_1} \text{ and } I_2 = \frac{C_2}{T_2} \tag{20}$$

We then have two equations for the Peukert Capacity, as in Eq. 3:

$$C_p = I_1^k \times T_1 \text{ and } C_p = I_2^k \times T_2 \tag{21}$$

However, since the Peukert Coefficient is Constant, the right hand sides of both parts of Eq. 21 are equal, and thus:

$$\begin{gathered} I_1^k T_1 = I_2^k T_2 \\ \left(\frac{I_1}{I_2}\right)^k = \frac{T_2}{T_1} \end{gathered} \tag{22}$$

Taking logs, and rearranging this gives:

$$K = \frac{\left(\log T_2 - \log T_1\right)}{\left(\log I_1 - \log I_2\right)} \tag{23}$$

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, Eq. 22 becomes:

$$I_1 = \frac{C_1}{T_1} = \frac{42}{10} = 4.2A \text{ and } I_1 = \frac{C_2}{T_2} = \frac{33.6}{1} = 33.6A \tag{24}$$

Putting these values into Eq. 23 gives:

$$k = \frac{\log 1 - \log 10}{\log 4.2 - \log 33.6} = 1.107 \tag{25}$$

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 Eq. 30, the gradient of the best-fit line of this graph is the Peukert Coefficient.

Lecture 33: Alternative and Novel Energy Sources

Alternative and Novel Energy Sources

Introduction

In addition to conventional electrical power sources for electric vehicles such as batteries and fuel cells, there is a range of alternative options including solar photovoltaics, winddriven generators, flywheels and supercapacitors. There are also older systems which may be important in the development of electric vehicles, particularly electric supply rails either with mechanical pick-ups or modern ones with an inductive supply. In this lecture, considering *stores* of electrical energy, energy *conversion* devices, and energy *transfer* systems.

The following topics are covered in this lecture:

- Solar Photovoltaics
- Flywheels
- Supercapacitor

Solar Photovoltaics

Photovoltaic cells are devices that convert sunlight or solar energy into direct current electricity. They are usually found as flat panels, and such panels are now a fairly common sight, on buildings and powering roadside equipment, to say nothing of being on calculators and similar electronic equipment. They can also come as thin films, which can be curved around a car body.

Solar radiation strikes the upper atmosphere with a value of $1300\mathrm{Wm}^{-2}$ but some of the radiation is lost in the atmosphere and by the time it reaches the Earth's surface it is less than $1000\mathrm{Wm}^{-2}$, normally called a 'standard sun'. Even in hot sunny climates solar radiation is normally less than this. Typical solar radiation on a flat plate constantly turned towards the sun will average around $750\mathrm{Wm}^{-2}$ on a clear day in the tropics and around $500\mathrm{Wm}^{-2}$ in more hazy climates. For a flat plate such as a solar panel placed on a car roof, the sun will strike the plate at differing angles as the sun moves around the sky, which halves the amount of energy falling on the plate.

The exact average will depend on the latitude, being larger on the equator and less at higher latitudes. Solar radiation is split into direct radiation which comes from the direction of the sun which is normally prominent on cloudless days, and indirect radiation which is solar radiation broken up by cloud and dust, comes from all directions and is prominent on cloudy days. Photovoltaic cells convert both types of radiation into electricity with an efficiency of conversion of around 14%. So the power which could be obtained from a photovoltaic panel will be less than $100\mathrm{Wm}^{-2}$ when tracking the sun, and around half of this for a fixed panel on a horizontal car roof.

There are two methods of using solar panels,

1. Onboard
2. Off-board the vehicle.

Clearly even if the whole of a car plan area were covered with cells only a very limited amount of power would be obtained. For example, a car of plan area $5\mathrm{m}^2$ would produce a maximum of around 375W at the panel output, and an average of around 188 W, giving 1.88 kWh of energy over a 10 hour day, equivalent to the energy stored in around 50 kg of lead acid batteries. This energy could be stored in a battery and used to power the vehicle for short commuter and shopping trips; but basically this amount of energy is insubstantial and would normally only give an impracticably limited range.

Solar panels mounted off-board could give as much power as needed. The electricity could either charge the vehicle battery from a suitable charging point or could be supplied to the vehicle via supply rails. The idea of a solar roof could be wasteful, in the sense that it is expensive and when the car is not being used the power will go to waste, unless of course it is used for some other purpose such as charging domestic batteries at a remote residence. The surplus power could be sold back to the grid in some cases.

Apart from the disadvantage of low power per square meter, solar panels are not cheap, costing around £4000 per peak kW, when bought in bulk. Bearing in mind that a peak kW is rarely achieved even in very sunny places, the actual cost per kW achieved is considerably more than £4000. Despite this, the idea of solar photovoltaic cells fitted to vehicles should not be written off entirely. The efficiency will improve and may one day in the future be as high as 50%. The cost of photovoltaic cells has already fallen dramatically and the long-term cost of solar photovoltaic panels is predicted to fall still further. Apart from supplying power to drive the vehicle, solar photovoltaic cells may be used for other useful purposes, such as compensating for natural battery self-discharge, and also for cooling or heating the car whilst at rest. A small fan powered by a photovoltaic roof panel could be used to draw air through a vehicle and keep it cool when parked in the sun.

Flywheels

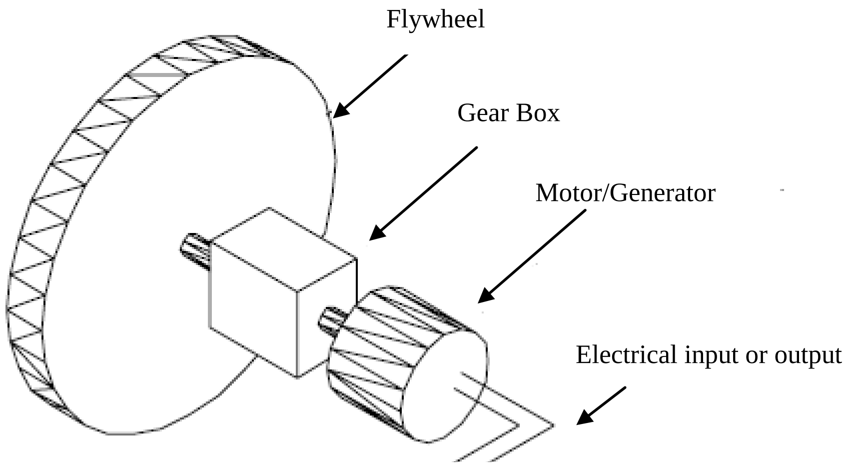
Introduction

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 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 1**, power electronics being required to match the generator output to a form where it can drive the vehicle motors. The flywheel can be re-accelerated, acting as a regenerative brake. Alternatively the flywheel can be connected to the vehicle wheels via a gearbox and a clutch.

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:

$$E = 0.5 I \omega^2 \tag{1}$$



1. To store energy current is supplied to the motor which accelerates the flywheel
2. To capture energy the flywheel drives the generator which supplies electrical energy

Fig. 1 Flywheel/generator arrangements

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 rad s^{-1} the energy released will be given by the formula:

$$\Delta E = 0.5 I(\omega_1^2 - \omega_2^2) \qquad (2)$$

If you 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 peripheral speed approaches the speed of light. Unfortunately as the flywheel 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 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 they 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 process around another axis. Again the behavior in an accident situation needs to be studied 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.

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 electric vehicle 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 electric vehicles, particularly in hybrids.

Super Capacitors

Capacitors are devices in which two conducting plates are separated by an insulator. An example is shown in **Figure 2**. 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:

$$Q = C \times V \tag{3}$$

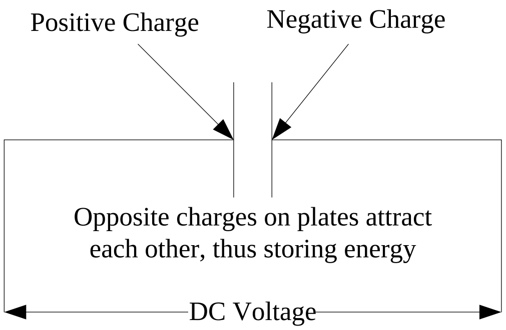


Fig. 2 Principle of the capacitor

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

$$E = \frac{1}{2} C V^2 \tag{4}$$

where E is the energy stored in Joules. The capacitance C of a capacitor in Farads will be given by the equation:

$$C = \varepsilon \frac{A}{d} \tag{5}$$

where ε is the 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 super capacitors 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, e.g. 10, 00, 000 $\mathrm{m^2kg^{-1}}$, and a 4, 000 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 V to 3 V. The problem with this is clear from Eq. 4; 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 cost, it brings other problems too.

If two capacitors C_1 and C_2 are connected in series then it is well known1 that the combined capacitance C is given by the formula:

$$\frac{1}{C}=\frac{1}{C_1}+\frac{1}{C_2} \tag{6}$$

So, for example, two 3 F capacitors 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 5**.

Another major problem with putting capacitors in series is that of charge equalization. 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 Eq. 3 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 equalization 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 the capacitors is the same.

These charge equalization 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 which have a current consumption of only 1mA. A Ragone plot comparing supercapacitors with batteries is shown in Fig. 3.

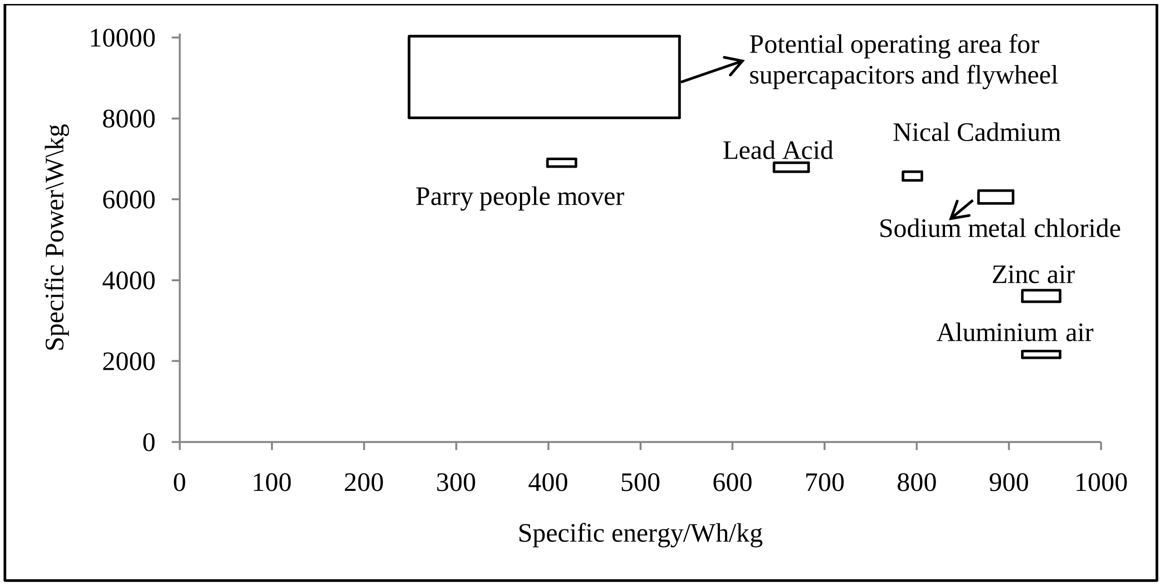


Fig. 3 Ragone plot of batteries, supercapacitors and flywheels

In many ways the characteristics of supercapacitors are like those of flywheels. They have relatively high specific power and relatively low specific energy. They can be used as the energy storage for regenerative braking. Although they could be used alone on a vehicle, they would be better used in a hybrid as devices for giving out and receiving energy rapidly during braking and accelerating afterwards, e.g. 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 super capacitors providing significant energy storage, and descriptions of these can be found in the literature.

Lecture 34: Fuel Cell

Fuel Cell

In this lecture the energy storage (fuel cell) is presented. The following topics are covered in this lecture:

- Fuel cell
- Issues in fuel cell
- Hydrogen fuel cell
- Fuel cell thermodynamics
- Main reasons for loss in voltage

Fuel Cell

Introduction

Fuel cells are hardly a new idea. They were invented in about 1840, but they are yet to really make their mark as a power source for electric vehicles. However, this might be set to change over the next 20 or 30 years. Certainly most of the major motor companies are spending very large sums of money developing fuel cell powered vehicles. The basic principle of the fuel cell is that it uses hydrogen fuel to produce electricity in a battery-like device to be explained in the next section. The basic chemical reaction is:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{1}$$

The product is thus water, and energy. Because the types of fuel cell likely to be used in vehicles work at quite modest temperatures ($\sim 85^{\circ}$C) there is no nitrous oxide produced by reactions between the components of the air used in the cell. A fuel cell vehicle could thus be described as zero-emission. Furthermore, because they run off a fairly normal chemical fuel (hydrogen), very reasonable energies can be stored, and the range of fuel cell vehicles is potentially quite satisfactory. They thus offer the only real prospect of a silent zero-emission vehicle with a range and performance broadly comparable with IC engine vehicles. It is not surprising then that there have, for many years, been those who have seen fuel cells as a technology that shows great promise, and could even make serious inroads into the domination of the internal combustion engine.

Main issues in the fuel cell

There are many problems and challenges for fuel cells to overcome before they become a commercial reality as a vehicle power source. The main problems centre on the following issues.

- *Cost:* Fuel cells are currently far more expensive than IC engines, and even hybrid IC/electric systems.
  - *Water management:* It is not at all self-evident why water management should be such an important and difficult issue with automotive fuel cells.
  - *Cooling:* The thermal management of fuel cells is actually rather more difficult than for IC engines.
  - *Hydrogen supply:* Hydrogen is the preferred fuel for fuel cells, but hydrogen is very difficult to store and transport. There is also the vital question of 'where does the hydrogen come from' these issues are so difficult and important, with so many rival solutions.

However, there is great hope that these problems can be overcome, and fuel cells can be the basis of less environmentally damaging transport.

Hydrogen Fuel Cells: Basic Principles

Electrode reactions

We have seen that the basic principle of the fuel cell is the release of energy following a chemical reaction between hydrogen and oxygen. The key difference between this and simply burning the gas is that the energy is released as an electric current, rather that heat. How is this electric current produced?

To understand this we need to consider the separate reactions taking place at each electrode. These important details vary for different types of fuel cell, but if we start with a cell based on an acid electrolyte, we shall consider the simplest and the most common type.

At the anode of an acid electrolyte fuel cell the hydrogen gas ionizes, releasing electrons and creating H^+ ions (or protons).

$$2H_2 \rightarrow 4H^+ + 4e^- \tag{2}$$

This reaction releases energy. At the cathode, oxygen reacts with electrons taken from the electrode, and H+ ions from the electrolyte, to form water.

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \qquad (3)$$

Clearly, for both these reactions to proceed continuously, electrons produced at the anode must pass through an electrical circuit to the cathode. Also, H^+ ions must pass through the electrolyte. An acid is a fluid with free H^+ ions, and so serves this purpose very well. Certain polymers can also be made to contain mobile H^+ ions.

Different electrolytes

The reactions given above may seem simple enough, but they do not proceed rapidly in normal circumstances. Also, the fact that hydrogen has to be used as a fuel is a disadvantage. To solve these and other problems many different fuel cell types have been tried. The different types are usually distinguished by the electrolyte that is used, though there are always other important differences as well.

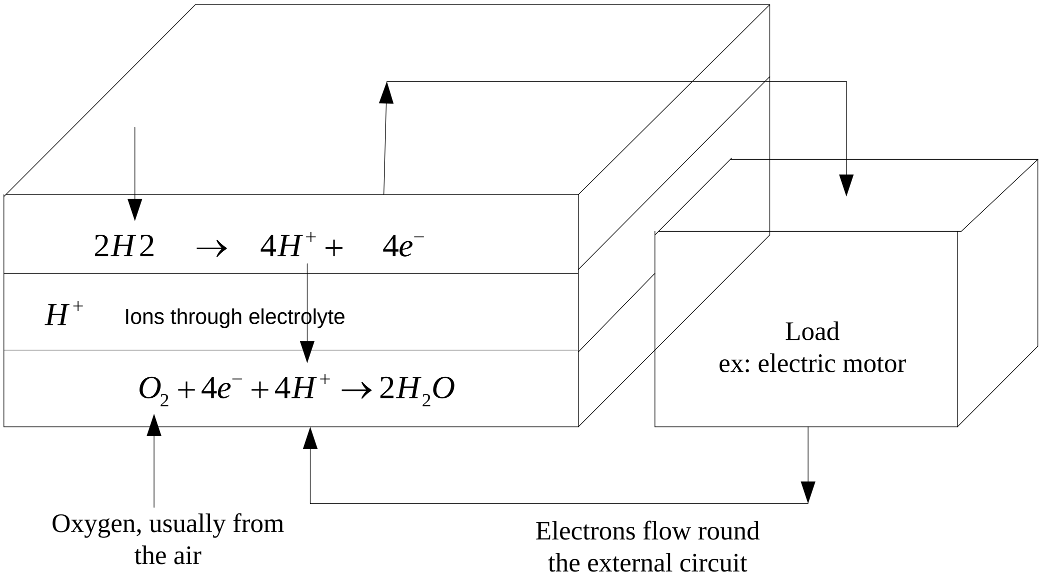


Fig. 1 The reactions at the electrodes, and the electron movement, in a fuel cell with an acid Electrolyte

Table I: Data for different types of fuel cell

Fuel cell type	Mobile ion	Operating temp.	Applications and notes
Alkaline (AFC)	OH^-	50–200°C	Used in space vehicles, e.g. Apollo, Shuttle.
Proton exchange membrane (PEMFC)	H^+	30-100°C	Vehicles and mobile applications, and for lower power CHP systems
Direct methanol(DMFC)	H^+	20-90°C	Suitable for portable electronic systems of low power, running for long times
Phosphoric acid (PAFC)	H^+	220°C	Large numbers of 200kW CHP systems in use
Molten carbonate (MCFC)	CO_3^{2-}	650°C	Suitable for medium to large scale CHP systems, up to MW capacity
Solid oxide (SOFC)	O^{2-}	500-1000°C	Suitable for all sizes of CHP systems, 2 kW to multi MW

The situation now is that six classes of fuel cell have emerged as viable systems for the present and near future. Basic information about these systems is given in Table I. As well as facing up to different problems, the various fuel types also try to play to the strengths of fuel cells in different ways. The PEM fuel cell capitalizes on the essential simplicity of the fuel cell. The electrolyte is a solid polymer, in which protons are mobile. The chemistry is the same as the acid electrolyte fuel cell of Fig. 1. With a solid and immobile electrolyte, this type of cell is inherently simple; it is the type that shows by far the most promise for vehicles, and is the type used on all the most impressive demonstration fuel cell vehicles. This type of fuel cell is the main focus of this chapter. PEM fuel cells run at quite low temperatures, so the problem of slow reaction rates has to be addressed by using sophisticated catalysts and electrodes. Platinum is the catalyst, but developments in recent years mean that only minute amounts are used, and the cost of the platinum is a small part of the total price of a PEM fuel cell.

One theoretically very attractive solution to the hydrogen supply problem is to use methanol1 as a fuel instead. This can be done in the PEM fuel cell, and such cells are called direct methanol fuel cells. ‘Direct’ because they use the methanol as the fuel as it is, in liquid form, as opposed to extracting the hydrogen from the methanol using one of the methods. Unfortunately these cells have very low power, and for the foreseeable future at least their use will be restricted to applications requiring slow and steady generation of electricity over long periods. A demonstration DMFC powered go-kart has been built, but really the only likely application of this type of cell in the near future is in the rapidly growing area of portable electronics equipment.

Although PEM fuel cells were used on the first manned spacecraft, the alkaline fuel cell was used on the Apollo and is used on the Shuttle Orbiter. The problem of slow reaction rate is overcome by using highly porous electrodes, with a platinum catalyst, and sometimes by operating at quite high pressures. Although some historically important alkaline fuel cells have operated at about 200◦C, they more usually operate below 100◦C. The alkaline fuel cell has been used by a few demonstration electric vehicles, always in hybrid systems with a battery. They can be made more cheaply than PEMFCs, but they are lower in power, and the electrolyte reacts with carbon dioxide in the air, which make terrestrial applications difficult.

Fuel cell electrodes

Fig. 2 is another representation of a fuel cell. Hydrogen is fed to one electrode, and oxygen, usually as air, to the other. A load is connected between the two electrodes, and current flows. However, in practice a fuel cell is far more complex than this. Normally the rate of reaction of both hydrogen and oxygen is very slow, which results in a low current, and so a low power. The three main ways of dealing with the slow reaction rates are: the use of suitable catalysts on the electrode, raising the temperature, and increasing the electrode area.

The first two can be applied to any chemical reaction. However, the third is special to fuel cells and is very important. If we take a reaction such as that of Eq. 3, we see that oxygen gas, and H^+ ions from the electrolyte, and electrons from the circuit are needed, all three together. This 'coming together' must take place on the surface of the electrode. Clearly, the larger the electrode area, the more scope there is for this to happen and the greater the current. This is very important. Indeed, electrode area is such a vital issue that the performance of a fuel cell design is often quoted in terms of the current *per* cm^2.

The structure of the electrode is also important. It is made highly porous so that the real surface area is much greater than the normal length × width. As well as being of a large surface area, and highly porous, a fuel cell electrode must also be coated with a catalyst layer. In the case of the PEMFC this is platinum, which is highly expensive. The catalyst thus needs to be spread out as finely as possible. This is normally done by supporting very fine particles of the catalyst on carbon particles.

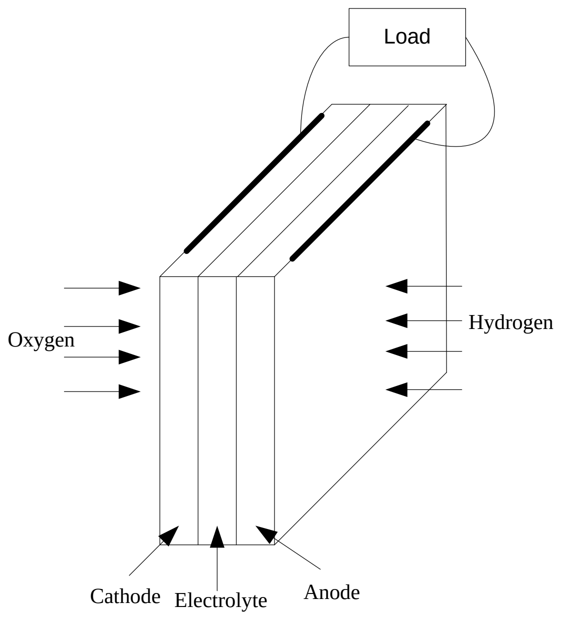


Fig. 2 Basic cathode-electrolyte-anode construction of a fuel cell.

The reactants need to be brought into contact with the catalyst, and a good electrical contact needs to be made with the electrode surface. Also, in the case of the cathode, the product water needs to be removed. These tasks are performed by the 'gas diffusion layer', a porous and highly conductive material such as carbon felt or carbon paper, which is layered on the electrode surface.

Fuel Cell Thermodynamics – Introduction

Fuel cell efficiency and efficiency limits

One of the attractions of fuel cells is that they are not heat engines. Their thermodynamics are different, and in particular their efficiency is potentially greater as they are not limited by the well-known Carnot limit that impinges on IC and other types of fuel burning engines. However, as we shall see, they do have their own limitations, and while fuel cells are often more efficient than IC engines, the difference is sometimes exaggerated.

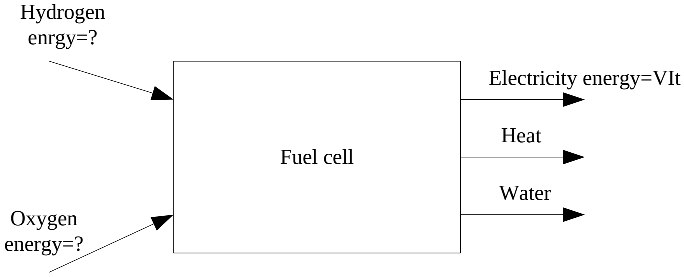


Fig. 3 Fuel cell inputs and outputs

At first we must acknowledge that the efficiency of a fuel cell is not straightforward to define. In some electrical power generating devices it is very clear what form of energy is being converted into electricity. With a fuel cell such energy considerations are much more difficult to visualize. The basic operation has already been explained, and the input and outputs are shown in Fig. 3. The electrical power and energy output are easily calculated from the well known formulas:

$$\text{Power} = VI \text{ and Energy} = VIt \tag{4}$$

However, the energy of the chemical inputs and output is not so easily defined. At a simple level we could say that it is the chemical energy of the H_2, O_2 and H_2O that is in question. The problem is that chemical energy is not simply defined, and terms such as enthalpy, Helmholtz function and Gibbs free energy are used. In recent years the useful term 'energy' has become quite widely used, and the concept is particularly useful in high temperature fuel cells, though we are not concerned with these here. There are also older (but still useful) terms such as calorific value.

In the case of fuel cells it is the Gibbs free energy that is important. This can be defined as the energy available to do external work, neglecting any work done by changes in pressure and/or volume. In a fuel cell the external work involves moving electrons round an external circuit; any work done by a change in volume between the input and output is not harnessed by the fuel cell. Energy is *all* the external work that can be extracted, including that due to volume and pressure changes. Enthalpy, simply put, is the Gibbs free energy plus the energy connected with the entropy. The enthalpy H, Gibbs free energy G and entropy S are connected by the well-known equation:

$$G = H - TS \tag{5}$$

The energy that is released by a fuel cell is the change in Gibbs energy before and after a reaction, so the energy released can be represented by the equation:

$$\Delta G = G_{outputs} - G_{inputs} \tag{6}$$

However, the Gibbs free energy change is *not constant*, but changes with temperature and state (liquid or gas). Table II below shows ΔG for the basic hydrogen fuel cell reaction for a number of different conditions. Note that the values are negative, which means that energy is released.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{7}$$

Table 2: ΔG for the reaction H_2 + 1_2 O2 → H_2O at various temperatures

Form of water product	Temperature (°C)	ΔG (kJ/mole)
Liquid	25	- 237.2
Liquid	80	-228.2
Gas	80	-226.1
Gas	100	-225.2
Gas	200	-220.4
Gas	400	-210.3
Gas	600	-199.6
Gas	800	-188.6
Gas	1000	-177.4

If there are no losses in the fuel cell, or as we should more properly say, if the process is reversible, then all this Gibbs free energy is converted into electrical energy. We could thus define the efficiency of a fuel cell as:

$$\frac{\text{electrical energy produced}}{\text{Gibbs free energy change}} \tag{8}$$

Since a fuel cell uses materials that are usually burnt to release their energy, it would make sense to compare the electrical energy produced with the heat that would be produced by burning the fuel. This is sometimes called the calorific value, though a more precise description is the change in enthalpy of formation. Its symbol is ΔH. As with the Gibbs free energy, the convention is that ΔH is negative when energy is released. So to get a good comparison with other fuel using technologies, the efficiency of the fuel cell is usually defined as:

$$\frac{\text{electrial energy produced per mole of fuel}}{-\Delta H} \tag{9}$$

However, even this is not without its ambiguities, as there are two different values that we can use for ΔH. For the burning of hydrogen:

$$\begin{gathered} H_2 + \frac{1}{2}O_2 \rightarrow H_2O \text{ (steam)} \\ \Delta H = \text{-}241.83\ kJ/mole \end{gathered} \tag{10}$$

whereas if the product water is condensed back to liquid, the reaction is:

$$\begin{gathered} H_2 + \frac{1}{2}O_2 \rightarrow H_2O \text{ (liquid)} \\ \Delta H = \text{-}285.84\ kJ/mole \end{gathered} \tag{11}$$

The difference between these two values for ΔH (44.01 kJ/mole) is the molar enthalpy of vaporization of water. The higher figure is called the higher heating value (HHV), and the lower, quite logically, the lower heating value (LHV). Any statement of efficiency should say whether it relates to the higher or lower heating value. If this information is not given, the LHV has probably been used, since this will give a higher efficiency figure.

We can now see that there is a limit to the efficiency, if we define it as in Eq. 4. The maximum electrical energy available is equal to the change in Gibbs free energy, so:

$$Maximum\ efficiency\ possible = \frac{\Delta G}{\Delta H} \times 100\% \tag{12}$$

This maximum efficiency limit is sometimes known as the thermodynamic efficiency. Table III gives the values of the efficiency limit, relative to the higher heating value, for a hydrogen fuel cell. The maximum voltage obtainable from a single cell is also given.

The graphs in Fig. 5 show how these values vary with temperature, and how they compare with the Carnot limit, which is given by the equation:

$$Carnot\ limit = \frac{T_1 - T_2}{T_1} \tag{13}$$

where T_1 is the higher temperature, and T_2 the lower, of the heat engine. The graph makes clear that the efficiency limit of the fuel cell is certainly not 100%, as some supporters of fuel cells occasionally claim. Indeed, above the 750°C the efficiency limit of the hydrogen fuel cell is actually less than for a heat engine. Nevertheless, the PEM fuel cells used in vehicles operate at about 80°C, and so their theoretical maximum efficiency is actually much better than for an IC engine.

Efficiency and the fuel cell voltage

A very useful feature of fuel cells is that their efficiency can be very easily found from their operating voltage. The reasoning behind this is as follows. If *one* mole of fuel is reacted in the cell, then *two* moles of electrons are pushed round the external circuit;

Table 3: *ΔG*, maximum EMF, and efficiency limit (HHV) for hydrogen fuel cells

Form of water product	Temp °C	*ΔG* kJ/mole−1	Max. EMF	Efficiency limit
Liquid	25	-237.2	1.23V	83%
Liquid	80	-228.2	1.18 V	80%
Gas	100	-225.3	1.17 V	79%
Gas	200	-220.4	1.14 V	77%
Gas	400	-210.3	1.09 V	74%
Gas	600	199.6	1.04 V	70%
Gas	800	-188.6	0.98 V	66%
Gas	1000	-177.4	0.92 V	62%

$$Energy = Ch\arg e \times Voltage \tag{14}$$

The Faraday constant *F* gives the charge on one mole of electrons. So, when one mole of hydrogen fuel is used in a fuel cell, if it were 100% efficient, as defined by Eq. 4, then we would be able to say that:

$$Energy = 2F \times V_{100\%} = \Delta H$$
$$and \text{ thus } V_{100\%} = \frac{\Delta H}{2F} \tag{15}$$

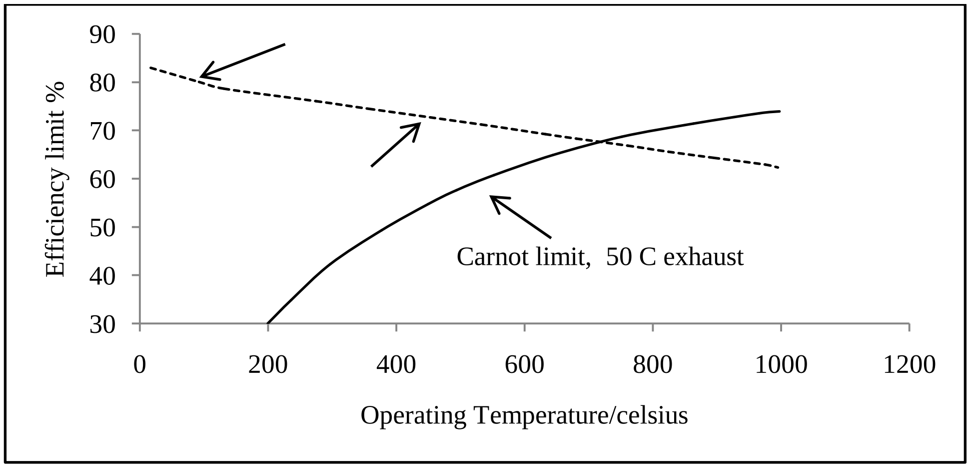


Fig. 5: Maximum hydrogen fuel cell efficiency at standard pressure, with reference to the higher heating value.

The two values for ΔH given above, we can easily calculate that the '100% efficient' voltage for a single cell is 1.48V if using the HHV or 1.25V if using the LHV. Now of course a fuel cell never is, and we have shown in the last section never can be, 100% efficient. The actual fuel cell voltage will be a lower value, which we can call V_c. Since voltage and electrical energy are directly proportional, it is clear that

$$Fuelcellefficiency = \frac{Vc}{V_{100\%}} = \frac{Vc}{1.48} \qquad (16)$$

Clearly it is very easy to measure the voltage of a fuel cell. In the case of a stack of many cells, remember that the voltage of concern is the average voltage one cell, so the system voltage should be divided by the number of cells. The efficiency can thus be found remarkably easily.

It is worth noting in passing that the maximum voltage of a fuel cell occurs when 100% of the Gibbs free energy is converted into electrical energy. Thus we have a 'sister' equation to Eq. 4, giving the maximum possible fuel cell voltage:

$$V_{\max} = \frac{\Delta G}{2F} \qquad (17)$$

This is also a very important fuel cell equation, and it was used to find the figures shown in the fourth column of Table III.

Practical fuel cell voltages

In practice the actual cell voltage is less than this. Now of course this applies to ordinary batteries too, as when current is drawn out of any electric cell the voltage falls, due to internal resistances. However, with a fuel cell this effect is more marked than with almost all types of conventional cell. **Figure 6** shows a typical voltage/current density curve for a good PEM fuel cell. It can be seen that the voltage is always less, and is often much less, than the 1.18V that would be obtained if all of the Gibbs energy were converted into electrical energy.

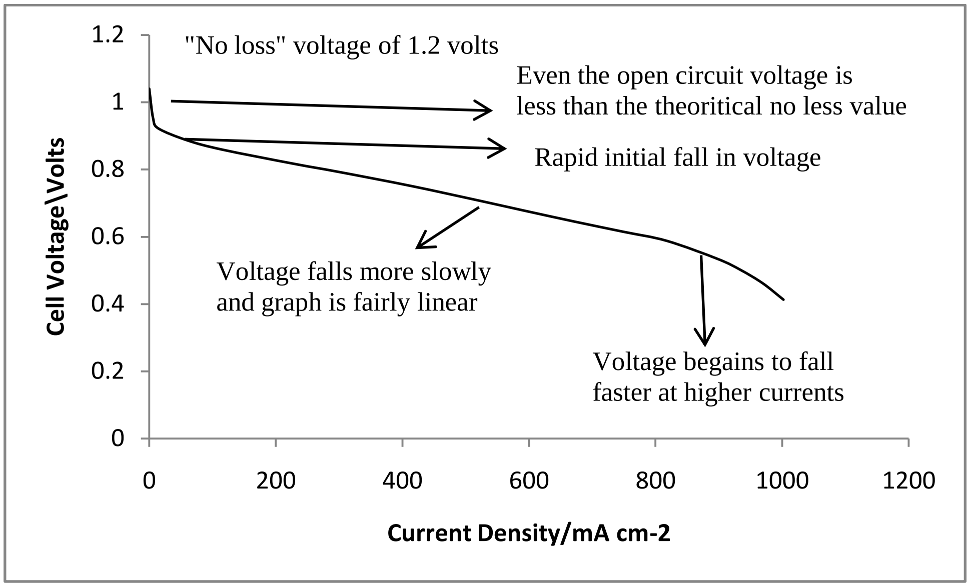


Fig. 6 Graph showing the voltage from a typical good quality PEM fuel cell operating on air at about 80◦C

There are three main reasons for this loss of voltage, as detailed below.

- The energy required to drive the reactions at the electrodes, usually called the activation energy, causes a voltage drop. This is especially a problem at the air cathode, and shows itself as a fairly constant voltage drop. This explains the initial fall in voltage even at quite low currents.
- The resistance of the electrolyte and the electrodes causes a voltage drop that more or less follows Ohm’s law, and causes the steady fall in voltage over the range of currents. This is usually called the Ohmic voltage loss.

- At very high currents, the air gets depleted of oxygen, and the remnant nitrogen gets in the way of supplying fresh oxygen. This result is a fall in voltage, as the electrodes are short of reactant. This problem causes the more rapid fall in voltage at higher currents, and is called mass transfer or concentration voltage loss.

The effect of pressure and gas concentration

The values for the changes in the Gibbs free energy given in Tables II and III all concern pure hydrogen and oxygen, at standard pressure, 100 kPa. However, as well as changing with temperature, as shown in these tables, the Gibbs energy changes with pressure and concentration.

A full treatment of these issues is beyond a book such as this, and it can easily be found elsewhere. Suffice to say that the relationship is given by a very important fuel cell equation derived from the work of Nernst. It can be expressed in many different forms, depending on what issue is to be analyzed. For example, if the change of system pressure is the issue, then the Nernst equation takes the form:

$$\Delta V = \frac{RT}{4F}\ln\left(\frac{P_2}{P_1}\right) \tag{18}$$

Where ΔV is the voltage increase if the pressure changes from P_1 to P_2. Other causes of voltage change are a reduction in voltage caused by using air instead of pure oxygen. The use of hydrogen fuel that is mixed with carbon dioxide, as is obtained from the ‘reforming’ of fuels such as petrol, methanol or methane, also causes a small reduction in voltage.

For high temperature fuel cells the Nernst equation predicts very well the voltage changes. However, with lower temperature cells, such as are used in electric vehicles, the changes are nearly always considerably greater than the Nernst equation predicts. This is because the ‘activation voltage drop’ mentioned in the last section is also quite strongly affected by issues such as gas concentration and pressure. This is especially the case at the air cathode.

The voltage increase resulting from a doubling of the system pressure would be:

$$\Delta V = \frac{8.314 \times (273+80)}{4 \times 96485} \ln(2) = 0.0053V \ per \ cell \tag{19}$$

However, in practice the voltage increase would typically be about 0.04 V, nearly ten times as much. Even so, we should note that the increase is still not large, and that there is considerable energy cost in running the system at higher pressure. Indeed, it is shown elsewhere that the energy gained from a higher voltage is very unlikely to be greater than the energy loss in pumping the air to higher pressure.