

EHV-Unit-2

Energy storage

Introduction to energy storage requirements in hybrid and electric vehicles:

“Energy storages” are defined as the devices that store energy, deliver energy outside (discharge), and accept energy from outside (charge).

There are several types of energy storages that have been proposed for electric vehicle (EV) and hybrid electric vehicle (HEV) applications. These energy storages, so far, mainly include chemical batteries, ultracapacitors or supercapacitors, ultrahigh-speed flywheels and the fuel cell.

There are a number of requirements for energy storage applied in an automotive application, such as specific energy, specific power, efficiency, maintenance requirement, management, cost, environmental adaptation and friendliness, and safety.

For allocation on an EV, specific energy is the first consideration since it limits the vehicle range. On the other hand, for HEV applications, specific energy becomes less important and specific power is the first consideration, because all the energy is from the energy source (engine or fuel cell) and sufficient power is needed to ensure vehicle performance, particularly during acceleration, hill climbing, and regenerative braking. Of course, other requirements should be fully considered in vehicle drive train development.

Characteristics of energy storage systems:

The appropriate selection of the ESSs for EV applications mainly depends on their characteristics, namely, capacity, total output power, discharge time, DOD, self-discharge, life cycle, efficiency, size, and cost.

The capacity of an ESS is defined as the total amount of energy available in this system, which is stored after full charge. The utilization of the capacity may vary from ESS to ESS in terms of self-discharge, DOD, and response time.

The characteristics of total power available in an ESS confine the specification of conversion system and load such that ESS can be discharged or recharged at its maximum value. The output and discharge of the power of ESS depend on the system response and demand. Therefore, the power is factorized with the rate of discharge or energy transmission according to the amount of time that it may need to extract the stored energy to deliver to the load as required.

The discharge time is the ratio of the amount of energy stored in an ESS to the maximum amount of power delivered from that system.

The self-discharge characteristic refers to the amount of energy lost over time when ESS is not in operation or is idle.

Life cycle refers to the durability of an ESS and depends on the number of times an ESS could deliver energy after every recharging. The life cycle depends on the materials that constitute the ESS and the level of safe operation.

Efficiency refers to the amount of energy that is delivered from the stored energy in an ESS.

ESS may be limited by several parameters, such as self-discharge, life cycle, properties of materials, energy conversion, and operating temperature.

The size of ESS is the crucial characteristic of an ESS for EV applications. A compact size corresponds to efficient performance of the ESS. The size specifies the high energy density of ESS in small mass and volume of the system. The cost is closely related with the size. Moreover, the capital cost of an ESS includes the storage system design, materials, and packaging, whereas the maintenance, loss, life span, and environmental issues are part of the operating cost..

The performance of ESSs differs from that of others on the basis of their characteristics. For efficient energy storage applications in EVs, high energy density, high power density, and a small size are essential characteristics for ESSs.

In addition, zero emission, negligible self discharge, low material corrosion due to chemical reaction, long cycle duration, high efficiency, and low maintenance are confirmed in manufacturing and selecting ESSs for EV powering. The ESS needs to respond quickly to climbing or hilling and remain steady at normal run with energy-power combination. For these purposes, hybrid ESSs are proposed for improving better ESSs in EV applications. Nowadays, R & D activities focus on the modification and advanced development of ESSs.

Issues and challenges of ESSs in EV applications

The present development of ESSs is satisfactory for EV energy storage and powering. Moreover, it reduces the demand for oil, CO₂ emissions, and GHGs. ESSs continuously mature with technological changes and improvements in certain applications. However, these applications still suffer from problems, such as raw material support and proper disposal, energy management, power electronics interface, sizing, safety measures, and cost. These issues of current ESSs are the primary challenges to advanced R & D actions for the advancement of energy storage in EV applications. The key issues are discussed with recommendations in the following sections.

Energy Storage

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.

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:

$$V = E - IR \quad (1)$$

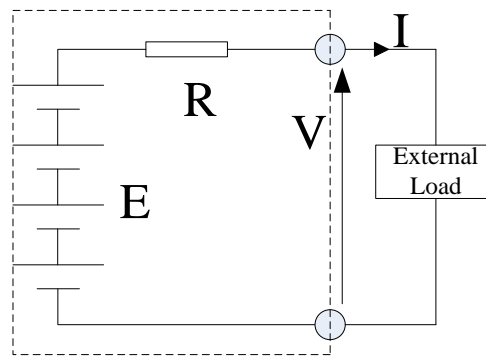


Fig. 1 Simple equivalent circuit model of a battery. This battery is composed of six cells

- *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.

$$\text{Energy in Whr} = V \times \text{Ahr} \quad (2)$$

- ***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:



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.

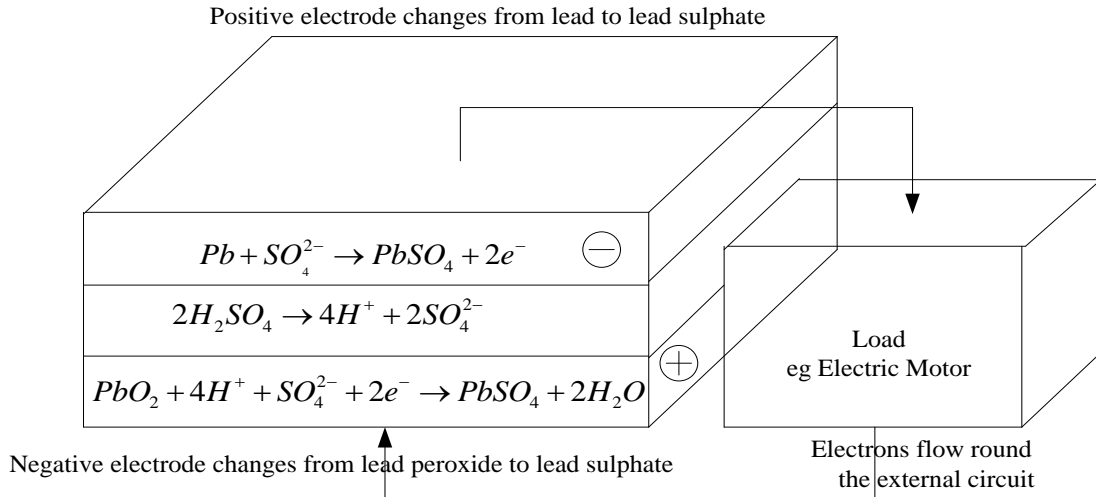
The lead acid battery is the most commonly used rechargeable battery in anything but the smallest of systems. The main reasons for this are that the main constituents (lead, sulphuric acid, a plastic container) are not expensive, that it performs reliably, and that it has a comparatively high voltage 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:

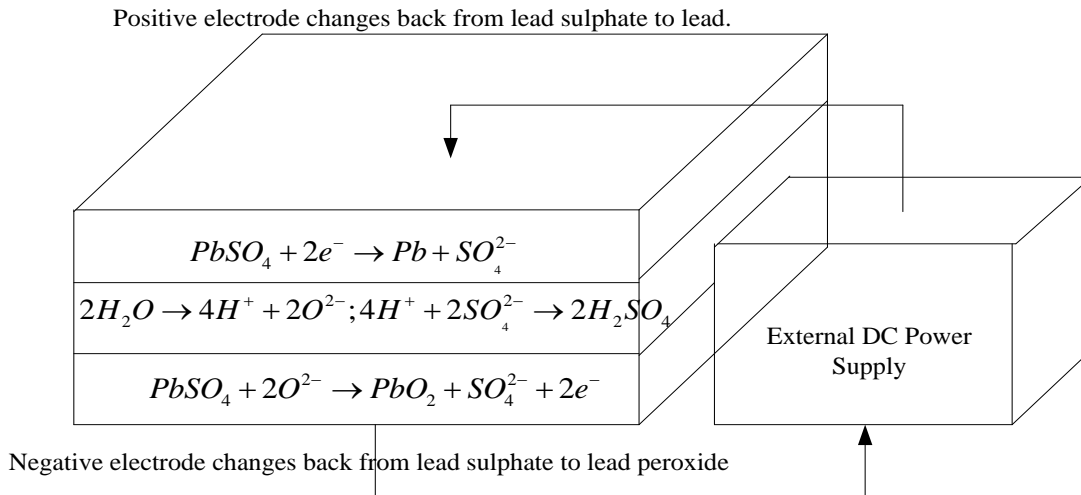
$$R = \text{No. of Cells} \times \frac{0.022}{C_{10}} \text{ Ohms} \quad (4)$$

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 sulphuric acid and gains water.



Reaction during the charging of the lead acid battery.
Note that the electrolyte sulphuric 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.

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.

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:

- Flywheels
- Supercapacitor

Flywheels

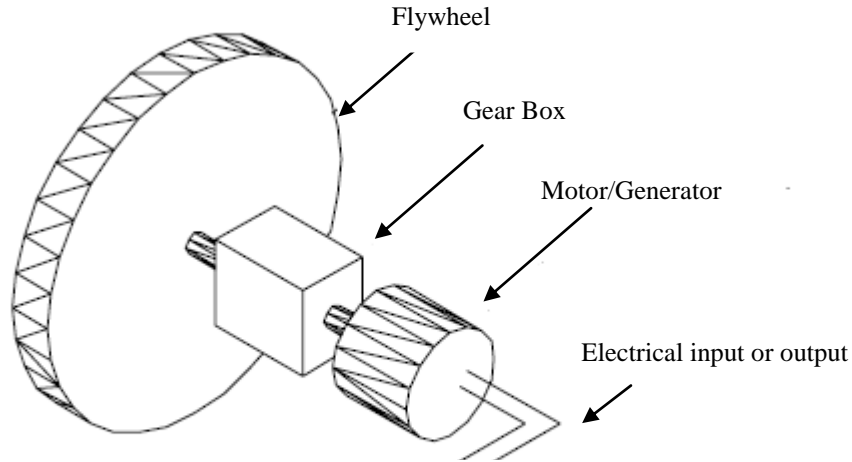
Introduction

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:

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



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:

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

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 precess 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:

$$Q = C \times V \quad (3)$$

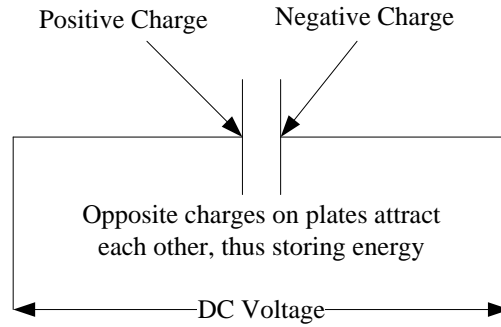


Fig. 2 Principle of the capacitor

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:

$$E = \frac{1}{2} CV^2 \quad (4)$$

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

$$C = \varepsilon \frac{A}{d} \quad (5)$$

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 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. $10,000,000 \text{ m}^2\text{kg}^{-1}$, and a $4,000 \text{ F}$ 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:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad (6)$$

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.

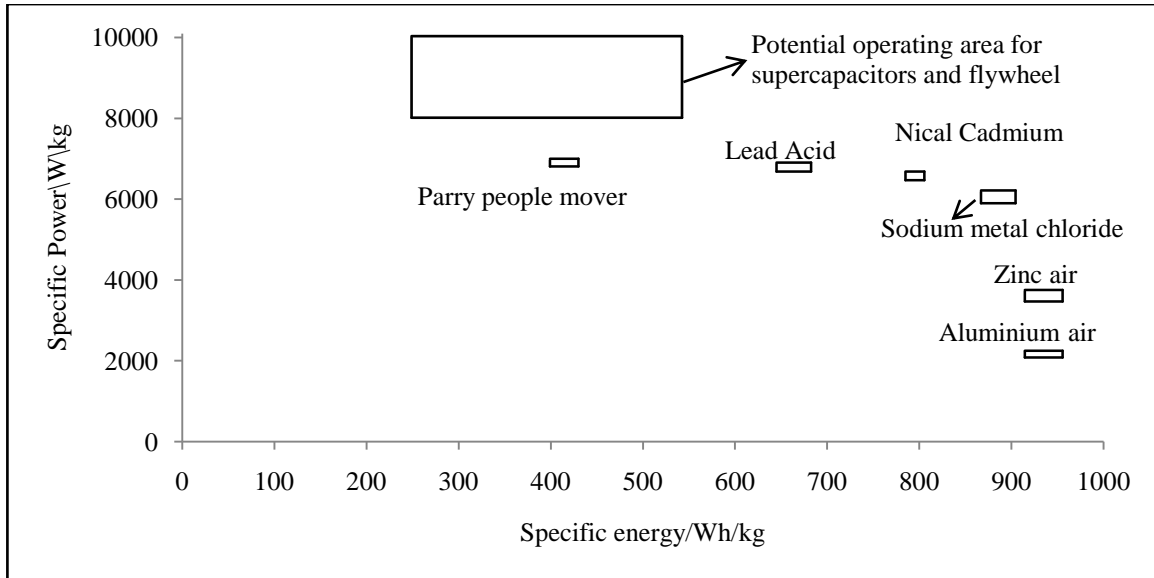


Fig. 3 Ragone plot of batteries, supercapacitors and flywheels

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 supercapacitors providing significant energy storage, and descriptions of these can be found in the literature.

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:



The product is thus water, and energy. Because the types of fuel cell likely to be used in vehicles work at quite modest temperatures ($\sim 85^\circ\text{C}$) 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

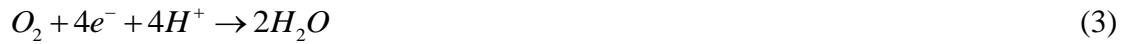
We have seen that the basic principle of the fuel cell is the release of energy following a chemical reaction between hydrogen and oxygen. The key difference between this and simply burning the gas is that the energy is released as an electric current, rather than heat. How is this electric current produced?

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).



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



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.

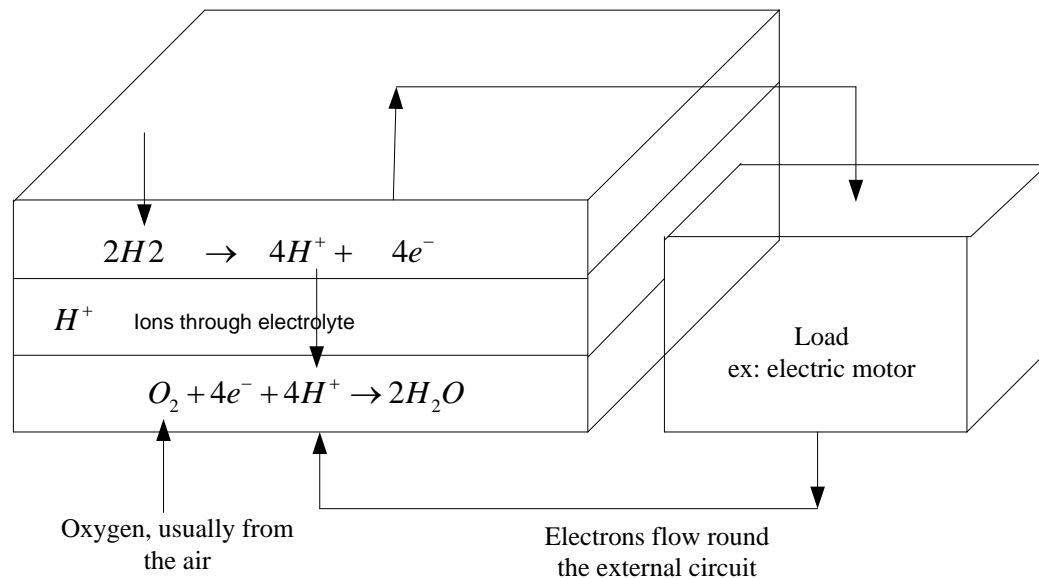


Fig. 1 The reactions at the electrodes, and the electron movement, in a fuel cell with an acid Electrolyte

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 methanol 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 cm²*.

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 \times 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.

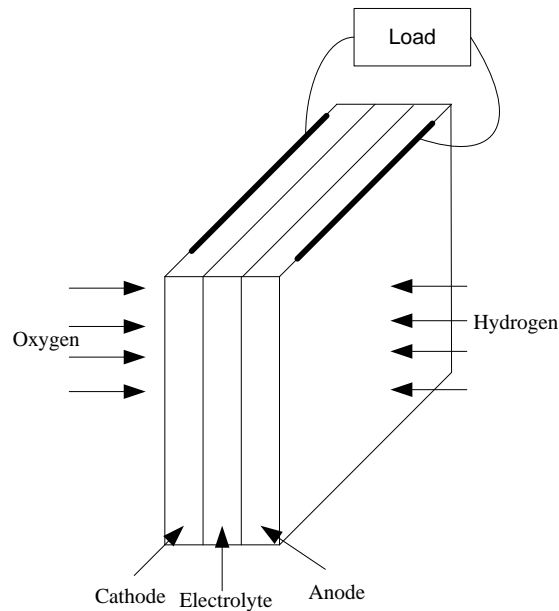


Fig. 2 Basic cathode-electrolyte-anode construction of a fuel cell.

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.

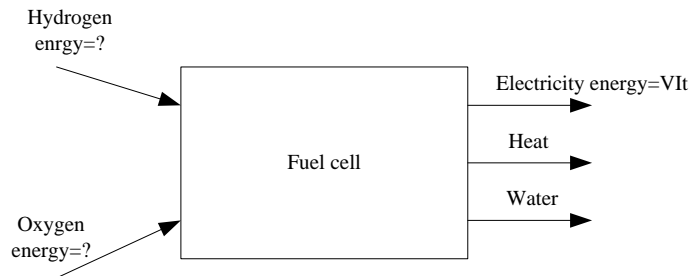


Fig. 3 Fuel cell inputs and outputs

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:

$$\text{Power} = VI \text{ and Energy} = VIt \quad (4)$$

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:

$$G = H - TS \quad (5)$$

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:

$$\Delta G = G_{\text{outputs}} - G_{\text{inputs}} \quad (6)$$

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.



Table 2: ΔG for the reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ 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:

$$\frac{\text{electrical energy produced}}{\text{Gibbs free energy change}} \quad (8)$$

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:

$$\frac{\text{electrical energy produced per mole of fuel}}{-\Delta H} \quad (9)$$

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:



$$\Delta H = -241.83 \text{ kJ / mole}$$

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



$$\Delta H = -285.84 \text{ kJ / mole}$$

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:

$$\text{Maximum efficiency possible} = \frac{\Delta G}{\Delta H} \times 100\% \quad (12)$$

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:

$$\text{Carnot limit} = \frac{T_1 - T_2}{T_1} \quad (13)$$

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%

$$\text{Energy} = \text{Charge } e \times \text{Voltage} \quad (14)$$

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:

$$\text{Energy} = 2F \times V_{100\%} = \Delta H$$

and thus $V_{100\%} = \frac{\Delta H}{2F}$ (15)

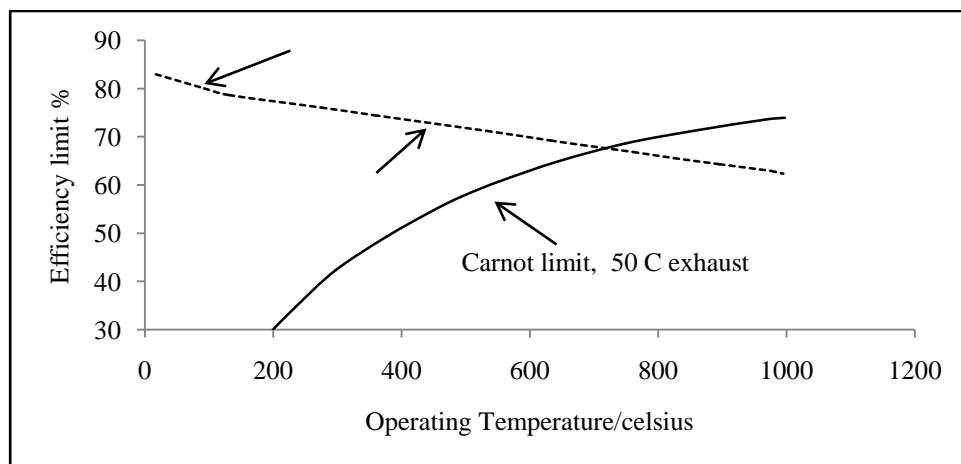


Fig. 5: Maximum hydrogen fuel cell efficiency at standard pressure, with reference to the higher heating value.

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

$$\text{Fuel cell efficiency} = \frac{V_c}{V_{100\%}} = \frac{V_c}{1.48} \quad (16)$$

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:

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

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.

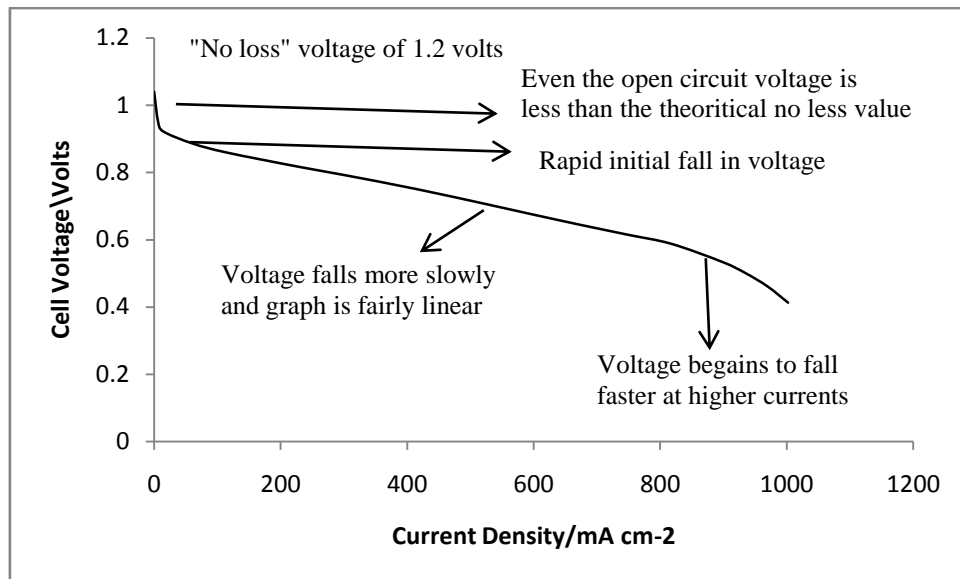


Fig. 6 Graph showing the voltage from a typical good quality PEM fuel cell operating on air at about 80°C

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:

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

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:

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

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.