

6

Hydrogen as a Fuel – Its Production and Storage

6.1 Introduction

In the previous chapter we outlined the operation of fuel cells and explained the main engineering problems with proton exchange membrane (PEM) fuel cells (PEMFCs). However, perhaps the most difficult problem was not addressed – how to obtain the hydrogen fuel. It should be said at this point that the question of how to supply hydrogen does not just concern fuel cell vehicles. In the previous chapter we alluded to the possibility (and indeed the practice) of running IC engines on hydrogen. A hydrogen-powered IC engine in a hybrid electrical system could also provide a system with very low pollution.

There is already a considerable infrastructure for the manufacture and supply of hydrogen. It is used in large quantities as a chemical reagent, especially for oil refining and petroleum processing. It is also produced in huge quantities for the manufacture of ammonia in the fertiliser industry. The great majority of this hydrogen is produced by steam reforming of natural gas, which is outlined below in Section 6.3.

However, when it comes to providing hydrogen on a smaller scale, to mobile systems like a vehicle, then many problems occur, to which no really satisfactory solutions have yet been found. There are many ways in which the problem could be solved, but it is as yet far from clear which will emerge as the winners. The different possibilities are shown in Figure 6.1.

In terms of infrastructure changes, the simplest method would be to adapt the current large-scale hydrogen production methods to a very small scale, and have ‘reformers’ onboard vehicles that produce hydrogen from currently standard fuels such as gasoline (petrol). This approach is also explained in Section 6.3.

One solution is to use the present production methods, and have the hydrogen produced in large central plants, or by electrolyzers, and stored and transported for fuel cell use as hydrogen. If such bulk hydrogen were produced by electrolyzers running off electricity produced from renewable sources, or by chemical means from biomass fuels, then this

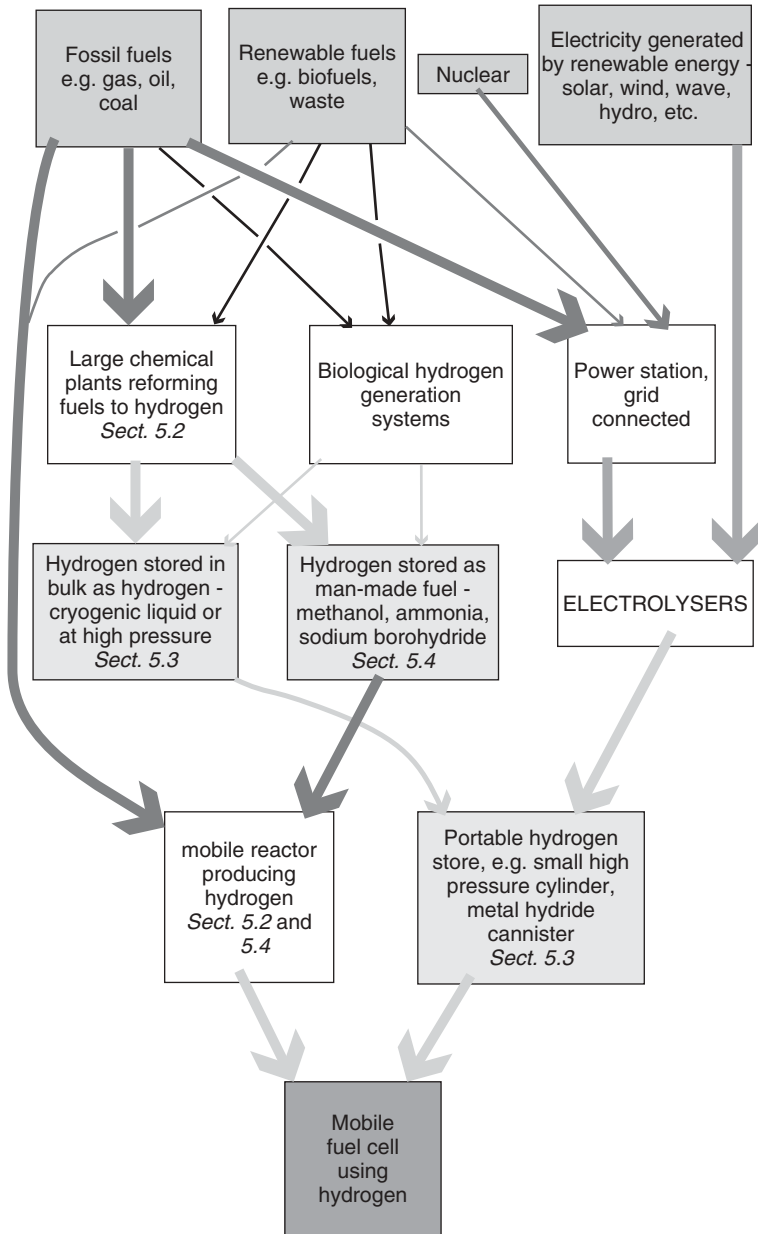


Figure 6.1 The supply of hydrogen to fuel-cell-powered vehicles can be achieved in many different ways



Figure 6.2 A hydrogen filling station. The bus in the picture is not electric, but uses a hydrogen-fuelled IC engine (Picture kindly supplied by MAN Nutzfahrzeuge A.G.)

would represent a system that was ‘carbon dioxide neutral’, and is the future as seen by the more optimistic.¹

In this scenario the bulk hydrogen would be stored at local filling stations, and vehicles would ‘fill up’ with hydrogen, much as they do now with diesel or petrol. Already a very few such filling stations exist, and one is shown in Figure 6.2. However, the storage of hydrogen in such stations, and even more so onboard the vehicle, is far from simple. The reasons for this are explained in Section 6.5. The problem is made more complex because some of the ways of storing hydrogen are so radically different. However, two distinct groups of methods can be identified. In one the hydrogen is stored simply as hydrogen – compressed, or liquefied, or held in some kind of ‘absorber’. The possible methods of doing this are explained in Section 6.5. This section also addresses the important issue of hydrogen safety.

In the second group of hydrogen storage methods the hydrogen is produced in large chemical plants, and is then used to produce hydrogen-rich chemicals or human-made fuels. Among these are ammonia and methanol. These ‘hydrogen carrier’ compounds can be made to give up their hydrogen much more easily than fossil fuels, and can be used in mobile systems. The most important of these compounds, and the ways they could be used, are explained in Section 6.5.

6.2 Hydrogen as a Fuel

Hydrogen has a specific energy of 33.3 kWh kg^{-1} whereas petrol has a specific energy of 12.3 kWh kg^{-1} and aviation fuel (kerosene) a specific energy of 12 kWh kg^{-1} . For the same energy content liquid hydrogen will therefore have a mass of 0.35 that of petrol.

¹ However, it has to be said that at the moment the great majority of hydrogen production involves the creation of carbon dioxide.

Despite its attractively high specific energy, hydrogen has a very low energy density. It is normally stored in pressurised tanks or it can be stored as liquid hydrogen at low temperature. The density of liquid hydrogen at normal temperature under 300 bar of pressure is 27 kg m^{-3} ; stored as liquid hydrogen its density is 70 kg m^{-3} . This contrasts with petrol which has a density of $700\text{--}750 \text{ kg m}^{-3}$.

The energy density of hydrogen pressurised at 300 bar will therefore be 899 kWh m^{-3} and liquid hydrogen 2331 kWh m^{-3} . This compares with petrol whose energy density is 9065 kWh m^{-3} . A fuel tank of hydrogen pressurised at 300 bar will therefore need to be 10 times the volume of a petrol tank and 3.89 times the volume of the equivalent petrol tank. (Gaseous hydrogen at NTP has a density of 0.09 kg m^{-3} and energy density of 3 kWh m^{-3} .)

6.3 Fuel Reforming

6.3.1 Fuel Cell Requirements

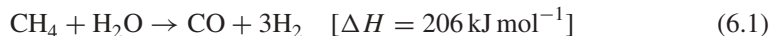
Fuel reforming is the process of taking the delivered fuel, such as fossil fuel gasoline or propane or methanol, and converting it to a form suitable for the PEMFC. This will never involve simply converting it to pure hydrogen; there will always be other substances present, particularly carbon compounds.

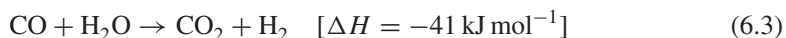
A particular problem with fuel reformers and PEMFCs is the presence of carbon monoxide. This has very severe consequences for this type of fuel cell. It ‘poisons’ the catalyst on the electrode, and its concentration must be kept lower than about 10 ppm. Carbon dioxide will always be present in the output of a reformer, and this poses no particular problems, except that it dilutes the fuel gas and slightly reduces the output voltage. Steam will also be present, but as we have seen in the previous chapter, this is advantageous for PEMFCs.

There is a very important problem that the presence of carbon dioxide in the fuel gas imposes on a fuel cell system. This is that it becomes impossible to use absolutely all of the hydrogen in the fuel cell. If the hydrogen is pure, then it can be simply connected to a fuel cell, and it will be drawn into the cell as needed. Nothing need ever come out of the fuel side of the system. When the fuel gas is impure, then it will need to be circulated through the system, with the hydrogen being used as it goes through, and with virtually 100% carbon dioxide gas at the exit. This makes for another feature of the cell that needs careful control. It also makes it important that there is still some hydrogen gas, even at the exit, otherwise the cells near the exit of the fuel flow path will not work well, as the hydrogen will be too dilute. This means that the systems described in this section will never have 100% fuel utilisation – some of it will always have to pass straight through the fuel cell stack.

6.3.2 Steam Reforming

Steam reforming is a mature technology, practised industrially on a large scale for hydrogen production. The basic reforming reactions for methane and octane C_8H_{18} are





The reforming reactions (6.1 and 6.2) and the associated ‘water–gas shift reaction’ (6.3) are carried out normally over a supported nickel catalyst at elevated temperatures, typically above 500°C. Over a catalyst that is active for reaction 6.1 or 6.2, reaction 6.3 nearly always occurs as well. The combination of the two reactions taking place means that the overall product gas is a mixture of carbon monoxide, carbon dioxide and hydrogen, together with unconverted fuel and steam. The actual composition of the product from the reformer is then governed by the temperature of the reactor (actually the outlet temperature), the operating pressure, the composition of the fuel and the proportion of steam fed to the reactor. Graphs and computer models using thermodynamic data are available to determine the composition of the equilibrium product gas for different operating conditions. Figure 6.3 is an example, showing the composition of the output at 1 bar, with methane as the fuel.

It can be seen that, in the case of reaction 6.1, there are three molecules of carbon monoxide and one molecule of hydrogen produced for every molecule of methane reacted. Le Chatelier’s principle therefore tells us that the equilibrium will be moved to the right (i.e. in favour of hydrogen) if the pressure in the reactor is kept low. Increasing the pressure will favour the formation of methane, since moving to the left of the equilibrium reduces the number of molecules.

Another feature of reactions 6.1 and 6.2 is that they are usually *endothermic*, which means that heat needs to be supplied to the reaction to drive it forward to produce hydrogen and carbon monoxide. Higher temperatures (up to 700°C) therefore favour hydrogen formation, as shown in Figure 6.3.

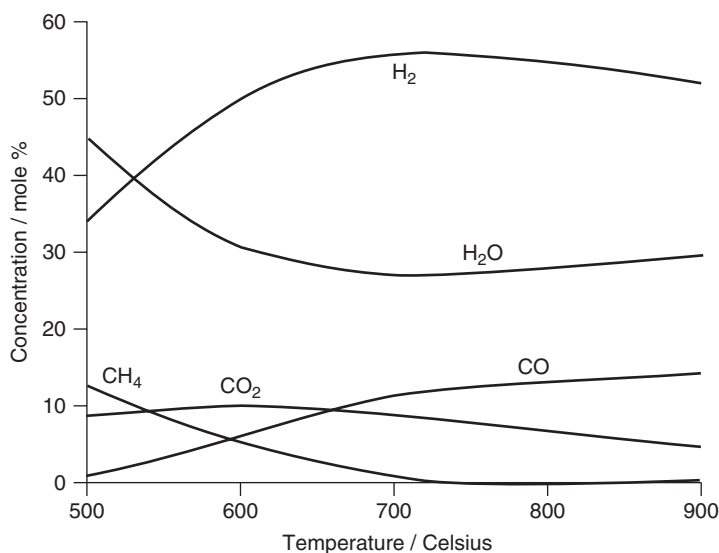


Figure 6.3 Equilibrium concentration of steam reformation reactant gases as a function of temperature. Note that at the temperature for optimum hydrogen production, there is also considerable quantities of carbon monoxide produced

It is important to note at this stage that although the shift reaction (6.3) does occur at the same time as steam reforming, at the high temperatures needed for hydrogen generation the equilibrium point for the reaction is well to the left of the equation. The result is that by no means all the carbon monoxide will be converted to carbon dioxide. For fuel cell systems that require low levels of carbon monoxide, further processing will be required. These reactions are the basis of the great majority of industrial hydrogen production, using natural gas (mainly methane) as the fuel.

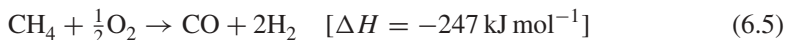
Hydrocarbons such as methane are not the only fuels suitable for steam reforming. Alcohols will also react in a steam reforming reaction, for example methanol:



The mildly endothermic steam reforming of methanol is one of the reasons why methanol is finding favour with vehicle manufacturers as a possible fuel for fuel cell vehicles, a point which is considered further in Section 6.6.2 below. Little heat needs to be supplied to sustain the reaction, which will readily occur at modest temperatures (e.g. 250 °C) over catalysts of mild activity such as copper supported on zinc oxide. Notice also that carbon monoxide does not feature as a principal product of methanol reforming. This makes methanol reformat particularly suited to PEMFCs, where carbon monoxide, even at the parts per million level, can cause substantial losses in performance due to poisoning of the platinum catalyst. However, it is important to note that although carbon monoxide does not feature in reaction 6.4, this does not mean that it is not produced at all. The water–gas shift reaction (6.3) is reversible, and carbon monoxide in small quantities is produced. The result is that the carbon monoxide removal methods described below are still needed with a methanol reformer used with a PEMFC.

6.3.3 Partial Oxidation and Autothermal Reforming

As an alternative to steam reforming, methane and other hydrocarbons may be converted to hydrogen for fuel cells via partial oxidation:



Partial oxidation can be carried out at high temperatures (typically 1200–1500 °C) without a catalyst, but this is not practical in small mobile systems. If the temperature is reduced and a catalyst employed then the process becomes known as catalytic partial oxidation (CPO). Catalysts for CPO tend to be supported platinum metal or nickel based.

It should be noted that reactions 6.5 and 6.6 produce less hydrogen per molecule of fuel than reaction 6.1 or 6.2. This means that partial oxidation (either non-catalytic or catalysed) is less efficient than steam reforming for fuel cell applications. Another disadvantage of partial oxidation occurs when air is used to supply the oxygen. This results in a lowering of the partial pressure of hydrogen at the fuel cell, because of the presence of the nitrogen, which further dilutes the hydrogen fuel. This in turn results in a lowering of the cell voltage, again resulting in a lowering of system efficiency. To offset these negative aspects, a key advantage of partial oxidation (POX) is that it does not require steam.

Autothermal reforming is another commonly used term in fuel processing. This usually describes a process in which both steam and oxidant (oxygen or more normally air) are fed with the fuel to a catalytic reactor. It can therefore be considered as a combination of POX and the steam reforming processes already described. The basic idea of autothermal reforming is that both the *endothermic* steam reforming reaction (6.1 or 6.2) and the *exothermic* POX reaction (6.5 or 6.6) occur together, so that no heat needs to be supplied or removed from the system. However, there is some confusion in the literature between the terms *partial oxidation* and *autothermal reforming*. Joensen and Rostrup-Nielsen have published a review which explains the issues in some detail (Joensen and Rostrup-Nielsen, 2002).

The advantages of autothermal reforming and CPO are that less steam is needed compared with conventional reforming and that all of the heat for the reforming reaction is provided by partial combustion of the fuel. This means that no complex heat management engineering is required, resulting in a simple system design. This is particularly attractive for mobile applications.

6.3.4 Further Fuel Processing – Carbon Monoxide Removal

A steam reformer reactor running on natural gas and operating at atmospheric pressure with an outlet temperature of 800 °C produces a gas comprising some 75% hydrogen, 15% carbon monoxide and 10% carbon dioxide on a dry basis. For the PEMFC, the carbon monoxide content must be reduced to much lower levels. Similarly, even the product from a methanol reformer operating at about 200 °C will have at least 0.1% carbon monoxide content, depending on pressure and water content. The problem of reducing the carbon monoxide content of reformed gas streams is thus very important.

We have seen that the water–gas shift reaction



takes place at the same time as the basic steam reforming reaction. However, the thermodynamics of the reaction are such that higher temperatures favour the production of carbon monoxide, and shift the equilibrium to the left. The first approach is thus to *cool* the product gas from the steam reformer and pass it through a reactor containing catalyst, which promotes the shift reaction. This has the effect of converting carbon monoxide into carbon dioxide. Depending on the reformat composition, more than one shift reactor may be needed, and two reactors is the norm. Such systems will give a carbon monoxide concentration of about 2500–5000 ppm, which exceeds the limit for PEMFCs by a factor of about 100. It is similar to the carbon monoxide content in the product from a methanol reformer.

For PEMFCs, further carbon monoxide removal is essential after the shift reactors. This is usually done in one of four ways:

1. In the **selective oxidation reactor** a small amount of air (typically around 2%) is added to the fuel stream, which then passes over a precious-metal catalyst. This catalyst preferentially absorbs the carbon monoxide, rather than the hydrogen, where it reacts with the oxygen in the air. As well as the obvious problem of cost, these units need to be very carefully controlled. There is the presence of hydrogen, carbon monoxide and oxygen, at an elevated temperature, with a noble-metal catalyst. Measures must be taken

to ensure that an explosive mixture is not produced. This is a special problem in cases where the flowrate of the gas is highly variable, such as with a PEMFC on a vehicle.

2. The **methanation** of the carbon monoxide is an approach that reduces the danger of producing explosive gas mixtures. The reaction is the opposite of the steam reformation reaction (6.1):



This method has the obvious disadvantage that hydrogen is being consumed, and so the efficiency is reduced. However, the quantities involved are small – we are reducing the carbon monoxide content from about 0.25%. The methane does not poison the fuel cell, but simply acts as a diluent. Catalysts are available which will promote this reaction so that at about 200 °C the carbon monoxide levels will be less than 10 ppm. The catalysts will also ensure that any unconverted methanol is reacted to methane, hydrogen or carbon dioxide.

3. **Palladium/platinum membranes** can be used to separate and purify the hydrogen. This is a mature technology that has been used for many years to produce hydrogen of exceptional purity. However, these devices are expensive.
4. **Pressure swing absorption (PSA)**. In this process, the reformer product gas is passed into a reactor containing absorbent material. Hydrogen gas is preferentially absorbed on this material. After a set time the reactor is isolated and the feed gas is diverted into a parallel reactor. At this stage the first reactor is depressurised, allowing pure hydrogen to desorb from the material. The process is repeated and the two reactors are alternately pressurised and depressurised. This process can be made to work well, but adds considerably to the bulk, cost and control problems of the system.

Currently none of these systems has established itself as the preferred option. They have the common feature that they add considerably to the cost and complexity of the fuel processing systems.

6.3.5 Practical Fuel Processing for Mobile Applications

The special features of onboard fuel processors for mobile applications are that they need:

- to be compact (both in weight and volume);
- to be capable of starting up quickly;
- to be able to follow demand rapidly and operate efficiently over a wide operating range;
- to be capable of delivering gas of low carbon monoxide content to the PEM stack;
- to emit very low levels of pollutants.

Over the past few years, research and development of fuel processing for mobile applications, as well as small-scale stationary applications, has mushroomed. Many organisations are developing proprietary technologies, but almost all of them are based on the options outlined above, namely steam reforming, CPO or autothermal reforming.

Companies such as Arthur D. Little have been developing reformers aimed at utilising gasoline-type hydrocarbons (Teagan, Bentley and Barnett, 1998). The company felt that the adoption of gasoline as a fuel for fuel cell vehicles (FCVs) would be likely to find

favour among oil companies, since the present distribution systems can be used. Indeed Shell has demonstrated its own CPO technology on gasoline and ExxonMobil in collaboration with GM has also been developing a gasoline fuel processor. Arthur D. Little spun out its reformer development into Epyx, which later teamed up with the Italian company De Nora to form the fuel cell company Nuvera. In the Nuvera fuel processing system the required heat of reaction for the reforming is provided by *in situ* oxidising a fraction of the feedstock in a combustion (POX) zone. A nickel-based catalyst bed following the POX zone is the key to achieving full fuel conversion for high efficiency. The POX section operates at relatively high temperatures (1100–1500 °C) whereas the catalytic reforming operates in the temperature range 800–1000 °C. The separation of the POX and catalytic zones allows a relatively pure gas to enter the reformer, permitting the system to accommodate a variety of fuels. Shift reactors (high and low temperature) convert the product gas from the reformer so that the exit concentration of carbon monoxide is less than 1%. As described earlier, an additional carbon monoxide removal stage is therefore needed to achieve the carbon monoxide levels necessary for a PEMFC. When designed for gasoline, the fuel processor also includes a compact desulfurisation bed integrated within the reactor vessel prior to the low-temperature shift.

Johnson Matthey has demonstrated its HotSpot reactor on reformulated gasoline (Ellis, Golunski and Petch, 2001). The company built a 10 kW fuel processor which met its technical targets, but it also addressed issues relating to mass manufacture. Johnson Matthey's work has identified areas that will require further work to enable gasoline reforming to become a commercial reality. These included:

- Hydrogen storage for startup and transients.
- An intrinsically safe afterburner design with internal temperature control and heat exchange that can cope with transients.
- Effect of additives on fuels.
- Better understanding of the issues relating to sulfur removal from fuels at source.
- Improved sulfur trapping and regeneration strategies.

GM has demonstrated its own gasoline fuel processor in a Chevrolet 2-10 pickup truck, billed as the world's first gasoline-fed fuel cell electric vehicle. With the rapid developments being made in this area it remains to be seen which of the various fuel processing systems will become economically viable in the future.

One way to sidestep all of the problems associated with onboard fuel processing is to make the fuel processing plant stationary, and to store the hydrogen produced, which can be loaded onto the mobile system as required. In fact, this may well be the preferred option for some applications, such as buses. However, as ever, solving one problem creates others, and the problems of storing hydrogen are quite severe. These are dealt with in Sections 6.5 and 6.6 below.

6.3.6 Energy Efficiency of Reforming

Not all the energy in the fuel from which the hydrogen is reformed goes into the hydrogen. The thermodynamic efficiency of reforming is between 70 and 85% (LHV basis) depending on the purity of the hydrogen product. The lower figure is likely for hydrogen reformed for fuel cells.

6.4 Energy Efficiency of Reforming

When we wish to steer away from fossil fuels the direct electrolysis of water from nuclear or electricity from alternative energy sources becomes more appropriate. Electrical energy generated from sources such as nuclear or solar energy will allow production of hydrogen without the release of carbon dioxide and hence the fuel does not give rise to carbon release and associated global warming at all.

Electrolysis is essentially a simple process. An electrical power source is connected to two electrodes typically made from some inert metal such as platinum or stainless steel, which are placed in the water. In a properly designed cell, hydrogen will appear at the cathode (the negatively charged electrode, where electrons are pumped into the water) and oxygen will appear at the anode (the positively charged electrode).

The ideal efficiency is known as the faradaic efficiency. The actual energy efficiency of water electrolysis varies widely, typically between 50 and 80%.

6.5 Hydrogen Storage I – Storage as Hydrogen

6.5.1 Introduction to the Problem

The difficulties arise because although hydrogen has one of the highest specific energies (energy per kilogram) – which is why it is the fuel of choice for space missions – its density is very low, and it has one of the lowest energy densities (energy per cubic metre). This means that to get a large mass of hydrogen into a small space very high pressures have to be used. A further problem is that, unlike other gaseous energy carriers, it is very difficult to liquefy. It cannot be simply compressed, in the way that LPG or butane can. It has to be cooled down to about 22 K, and even in liquid form its density is really very low, 71 kg m^{-3} .

Although hydrogen can be stored as a compressed gas or a liquid, there are other methods that are being developed. Chemical methods can also be used. These are considered in the next section. The methods of storing hydrogen that will be described in this section are:

- compression in gas cylinders;
- storage as a cryogenic liquid;
- storage in a metal absorber – as a reversible metal hydride;
- storage in carbon nanofibres.

None of these methods are without considerable problems, and in each situation their advantages and disadvantages will play out differently. However, before considering them in detail we must address the vitally important issue of safety in connection with storing and using hydrogen.

6.5.2 Safety

Hydrogen is a unique gaseous element, possessing the lowest molecular weight of any gas. It has the highest thermal conductivity, velocity of sound, mean molecular velocity and the lowest viscosity and density of all gases. Such properties lead hydrogen to have a leak rate through small orifices faster than all other gases. Hydrogen leaks 2.8 times

Table 6.1 Properties relevant to safety for hydrogen and two other commonly used gaseous fuels

	Hydrogen	Methane	Propane
Density (kg m^{-3} at NTP)	0.084	0.65	2.01
Ignition limits in air (vol % at NTP)	4.0–77	4.4–16.5	1.7–10.9
Ignition temperature ($^{\circ}\text{C}$)	560	540	487
Minimum ignition energy in air (MJ)	0.02	0.3	0.26
Maximum combustion rate in air (m s^{-1})	3.46	0.43	0.47
Detonation limits in air (vol %)	18–59	6.3–14	1.1–1.3
Stoichiometric ratio in air	29.5	9.5	4.0

faster than methane and 3.3 times faster than air. In addition hydrogen is a highly volatile and flammable gas, and in certain circumstances hydrogen and air mixtures can detonate. The implications for the design of fuel cell systems are obvious, and safety considerations must feature strongly.

Table 6.1 gives the key properties relevant to safety of hydrogen and two other gaseous fuels widely used in homes, leisure and business – namely, methane and propane. From this table the major problem with hydrogen appears to be the minimum ignition energy, apparently indicating that a fire could be started very easily. However, all these energies are in fact very low, lower than those encountered in most practical cases. A spark can ignite any of these fuels. Furthermore, against this must be set the much higher minimum concentration needed for detonation: 18% by volume. The lower concentration limit for ignition is much the same as for methane, and a considerably lower concentration of propane is needed. The ignition temperature for hydrogen is also noticeably higher than for the other two fuels.

Hydrogen therefore needs to be handled with care. Systems need to be designed with the lowest possible chance of any leaks, and should be monitored for such leaks regularly. However, it should be made clear that, all things considered, hydrogen is no more dangerous, and in some respects it is rather less dangerous, than other commonly used fuels.

6.5.3 *The Storage of Hydrogen as a Compressed Gas*

Storing hydrogen gas in pressurised cylinders is the most technically straightforward method, and the most widely used for small amounts of the gas. Hydrogen is stored in this way at thousands of industrial, research and teaching establishments and in most locations local companies can readily supply such cylinders in a wide range of sizes. However, in these applications the hydrogen is nearly always a chemical reagent in some analytical or production process. When we consider using and storing hydrogen in this way as an energy vector, then the situation appears less satisfactory.

Two systems of pressurised storage are compared in Table 6.2. The first is a standard steel alloy cylinder at 200 bar, of the type commonly seen in laboratories. The second is for larger scale hydrogen storage on a bus, as described by Zieger (1994). This tank is constructed with an aluminium inner liner 6 mm thick, around which is wrapped a composite of aramide fibre and epoxy resin. This material has a high ductility, which

Table 6.2 Comparative data for two cylinders used to store hydrogen at high pressure. The first is a conventional steel cylinder, the second a larger composite tank for use on a hydrogen-powered bus

	21 steel, 200 bar	147 l composite, 300 bar
Mass of empty cylinder (kg)	3.0	100
Mass of hydrogen stored (kg)	0.036	3.1
Storage efficiency (% mass H ₂) (%)	1.2	3.1
Specific energy (kWh kg ⁻¹)	0.47	1.2
Volume of tank (approximately)	2.21 (0.0022 m ³)	220 l (0.22 m ³)
Mass of H ₂ per litre (kg l ⁻¹)	0.016	0.014

gives it good burst behaviour, in that it rips apart rather than disintegrating into many pieces. The burst pressure is 1200 bar, though the maximum pressure used is 300 bar.

The larger scale storage system is, as expected, a great deal more efficient. However, this is slightly misleading. These large tanks have to be held in the vehicle, and the weight needed to do this should be taken into account. In the bus described by Zieger (1994), which used hydrogen to drive an IC engine, 13 of these tanks were mounted in the roof space. The total mass of the tanks and the bus structure reinforcements is 2550 kg or 196 kg per tank. This brings down the ‘storage efficiency’ of the system to 1.6%, not so very different from the steel cylinder. Another point is that in both systems we have ignored the weight of the connecting valves and of any pressure-reducing regulators. For the 21 steel cylinder system this would typically add about 2.15 kg to the mass of the system, and reduce the storage efficiency to 0.7% (Kahrom, 1999).

The reason for the low mass of hydrogen stored, even at such very high pressures, is of course its low density. The density of hydrogen gas at normal temperature and pressure is 0.084 kg m⁻³, compared with air, which is about 1.2 kg m⁻³. *Usually less than 2% of the storage system mass is actually hydrogen itself.*

The metal that the pressure vessel is made from needs very careful selection. Hydrogen is a very small molecule, of high velocity, and so it is capable of diffusing into materials that are impermeable to other gases. This is compounded by the fact that a very small fraction of the hydrogen gas molecules may dissociate on the surface of the material. Diffusion of atomic hydrogen into the material may then occur, which can affect the mechanical performance of materials in many ways. Gaseous hydrogen can build up in internal blisters in the material, which can lead to crack promotion (hydrogen-induced cracking). In carbonaceous metals such as steel the hydrogen can react with carbon forming entrapped CH₄ bubbles. The gas pressure in the internal voids can generate an internal stress high enough to fissure, crack or blister the steel. The phenomenon is well known and is termed hydrogen embrittlement. Certain chromium-rich steels and Cr–Mo alloys have been found that are resistant to hydrogen embrittlement. Composite reinforced plastic materials are also used for larger tanks, as has been outlined above.

As well as the problem of very high mass, there are considerable safety problems associated with storing hydrogen at high pressure. A leak from such a cylinder would generate very large forces as the gas is propelled out. It is possible for such cylinders to become

essentially jet-propelled torpedoes, and to inflict considerable damage. Furthermore, vessel fracture would most likely be accompanied by autoignition of the released hydrogen and air mixture, with an ensuing fire lasting until the contents of the ruptured or accidentally opened vessel are consumed (Hord, 1978). Nevertheless, this method is widely and safely used, provided the safety problems, especially those associated with the high pressure, are avoided by correctly following the due procedures. In vehicles, for example, pressure-relief valves or rupture discs are fitted which will safely vent gas in the event of a fire for instance. Similarly, pressure regulators attached to hydrogen cylinders are fitted with flame-traps to prevent ignition of the hydrogen.

The main advantages of storing hydrogen as a compressed gas are:

- simplicity;
- indefinite storage time;
- no purity limits on the hydrogen.

Designs for very high-pressure cylinders can be incorporated into vehicles of all types. In the fuel cell bus of Figure 1.17 they are in the roof. Figure 6.4 shows the design of a modern very high-pressure hydrogen storage system by General Motors, and its location in the fuel-cell-powered vehicle can be seen in the picture in the background.

6.5.4 Storage of Hydrogen as a Liquid

The storage of hydrogen as a liquid (commonly called LH₂), at about 22 K, is currently the only widely used method of storing large quantities of hydrogen. A gas cooled to the liquid state in this way is known as a *cryogenic liquid*. Large quantities of cryogenic hydrogen are currently used in processes such as petroleum refining and ammonia production. Another notable user is NASA, which has huge 3200 m³ (850 000 US gal) tanks to ensure a continuous supply for the space programme.

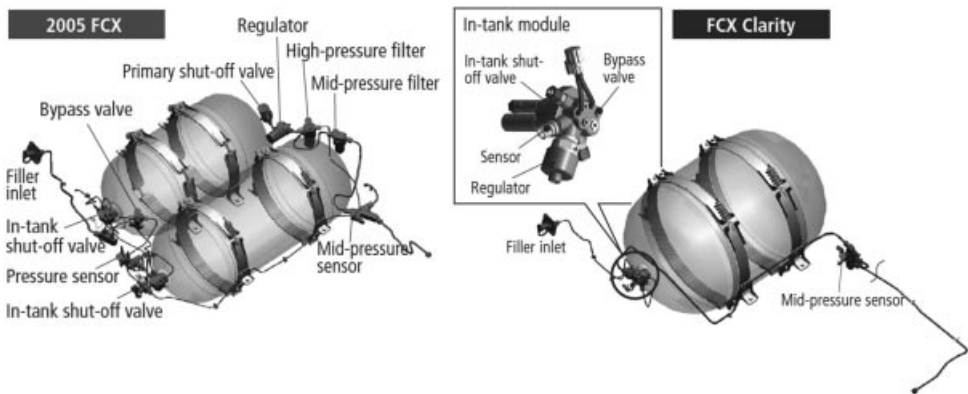


Figure 6.4 Honda pressurised hydrogen gas cylinder (Reproduced with permission from Honda Motor)

The hydrogen container is a large, strongly reinforced vacuum (or Dewar) flask. The liquid hydrogen will slowly evaporate, and the pressure in the container is usually maintained below 3 bar, though some larger tanks may use higher pressures. If the rate of evaporation exceeds the demand, then the tank is occasionally vented to make sure the pressure does not rise too high. A spring-loaded valve will release, and close again when the pressure falls. The small amounts of hydrogen involved are usually released to the atmosphere, though in very large systems it may be vented out through a flare stack and burnt. As a backup safety feature a rupture disc is usually also fitted. This consists of a ring covered with a membrane of controlled thickness, so that it will withstand a certain pressure. When a safety limit is reached, the membrane bursts, releasing the gas. However, the gas will continue to be released until the disc is replaced. This will not be done till all the gas is released and the fault rectified.

When the LH₂ tank is being filled, and when fuel is being withdrawn, it is most important that air is not allowed into the system, otherwise an explosive mixture could form. The tank should be purged with nitrogen before filling.

Although tanks are usually used to store large quantities of hydrogen, considerable work has gone into the design and development of LH₂ tanks for cars, though this has not been directly connected with fuel cells. BMW, among other automobile companies, has invested heavily in hydrogen-powered IC engines, and these have nearly all used LH₂ as the fuel. Such tanks have been through very thorough safety trials. The tank used in BMW's hydrogen-powered cars is cylindrical in shape, and is of the normal double-wall, vacuum or Dewar flask type of construction. The walls are about 3 cm thick, and consist of 70 layers of aluminium foil interlaced with fibre-glass matting. The maximum operating pressure is 5 bar. The tank stores 120 l of cryogenic hydrogen. The density of LH₂ is very low, about 71 kg m⁻³, so 120 l is only 8.5 kg (Reister and Strobl, 1992). The key figures are given in Table 6.3.

The hydrogen fuel feed systems used for car engines cannot normally be applied unaltered to fuel cells. One notable difference is that in LH₂ power engines the hydrogen is often fed to the engine still in the liquid state. If the hydrogen is a gas, then being at a low temperature is an advantage, as this allows a greater mass of fuel/air mixture into the engine. For fuel cells, the hydrogen will obviously need to be a gas, and pre-heated as well. However, this is not a very difficult technical problem, as there is plenty of scope for using waste heat from the cell via heat exchangers.

One of the problems associated with cryogenic hydrogen is that the liquefaction process is very energy intensive. Several stages are involved. The gas is firstly compressed and

Table 6.3 Details of a cryogenic hydrogen container suitable for cars

Mass of empty container	51.5 kg
Mass of hydrogen stored	8.5 kg
Storage efficiency (% mass H ₂)	14.2%
Specific energy	5.57 kWh kg ⁻¹
Volume of tank (approximately)	0.2 m ³
Mass of H ₂ per litre	0.0425 kg l ⁻¹

then cooled to about 78 K using liquid nitrogen. The high pressure is then used to cool the hydrogen further by expanding it through a turbine. An additional process is needed to convert the hydrogen from the isomer where the nuclear spins of both atoms are parallel (*ortho*-hydrogen) to that where they are anti-parallel (*para*-hydrogen). This process is exothermic, and if allowed to take place naturally would cause boil-off of the liquid. According to figures provided by a major hydrogen producer, and given by Eliasson and Bossel (2002), the energy required to liquefy the gas under the *very best of circumstances* is about 25% of the specific enthalpy or heating value of the hydrogen. This is for modern plants liquefying over 1000 kg h^{-1} . For plants working at about 100 kg h^{-1} , hardly a small rate, the proportion of the energy lost rises to about 45%. In overall terms then, this method is a highly inefficient way of storing and transporting energy.

In addition to the regular safety problems with hydrogen, there are a number of specific difficulties concerned with cryogenic hydrogen. Frostbite is a hazard of concern. Human skin can easily become frozen or torn if it comes into contact with cryogenic surfaces. All pipes containing the fluid must be insulated, as must any parts in good thermal contact with these pipes. Insulation is also necessary to prevent the surrounding air from condensing on the pipes, as an explosion hazard can develop if liquid air drips onto nearby combustibles. Asphalt, for example, can ignite in the presence of liquid air. (Concrete paving is used around static installations.) Generally, though, the hazards of hydrogen are somewhat less with LH_2 than with pressurised gas. One reason is that if there is a failure of the container, the fuel tends to remain in place and vent to the atmosphere more slowly. Certainly, LH_2 tanks have been approved for use in cars in Europe.

6.5.5 Reversible Metal Hydride Hydrogen Stores

The reader might well question the inclusion of this method in this section, rather than with the chemical methods that follow. However, although the method is chemical in its operation, that is not in any way apparent to the user. No reformers or reactors are needed to make the systems work. They work exactly like a hydrogen ‘sponge’ or ‘absorber’. For this reason the method is included here.

Certain metals, particularly mixtures (alloys) of titanium, iron, manganese, nickel, chromium and others, can react with hydrogen to form a metal hydride in a very easily controlled reversible reaction. The general equation is



To the right, reaction 6.8 is mildly exothermic. To release the hydrogen then, small amounts of heat must be supplied. However, metal alloys can be chosen for the hydrides so that the reaction can take place over a wide range of temperatures and pressures. In particular, it is possible to choose alloys suitable for operating at around atmospheric pressure, and at room temperature.

The system works as follows. Hydrogen is supplied at a little above atmospheric pressure to the metal alloy, inside a container. Reaction 6.8 proceeds to the right, and the metal hydride is formed. This is mildly exothermic, and in large systems some cooling will need to be supplied, but normal air cooling is often sufficient. This stage will take a few minutes, depending on the size of the system, and if the container is cooled. It will take place at approximately constant pressure.

Once all the metal has reacted with the hydrogen, then the pressure will begin to rise. This is the sign to disconnect the hydrogen supply. The vessel, now containing the metal hydride, will then be sealed. Note that the hydrogen is only stored at modest pressure, typically up to 5 bar.

When the hydrogen is needed, the vessel is connected to, for example, the fuel cell. Reaction 6.8 then proceeds to the left, and hydrogen is released. If the pressure rises above atmospheric, the reaction will slow down or stop. The reaction is now endothermic, so energy must be supplied. It is supplied by the surroundings – the vessel will cool slightly as the hydrogen is given off. It can be warmed slightly to increase the rate of supply, using, for example, warm water or the air from the fuel cell cooling system.

Once the reaction has completed, and all the hydrogen has been released, then the whole procedure can be repeated. *Note that we have already met this process*, when we looked at the metal hydride battery in Chapter 3; the same process is used to store hydrogen directly on the negative electrode.

Usually several hundred charge/discharge cycles can be completed. However, rather like rechargeable batteries, these systems can be abused. For example, if the system is filled at high pressure, the charging reaction will proceed too fast, and the material will get too hot and will be damaged. Also, another important problem is that the containers are damaged by impurities in the hydrogen, because the metal absorbers will react permanently with them. So a high-purity hydrogen, at least 99.999% pure, *must* be used.

Although the hydrogen is not stored at pressure, the container must be able to withstand a reasonably high pressure, as it is likely to be filled from a high-pressure supply, and allowance must be made for human error. For example, the unit shown in Figure 6.5 will be fully charged at a pressure of 3 bar, but the container can withstand 30 bar. The container will also need valves and connectors. Even taking all these into account, impressive practical devices can be built. Table 6.4 gives details of the small 20 SL (standard litre)



Figure 6.5 Metal hydride stores can be made quite small, as this example shows

Table 6.4 Details of a small metal hydride hydrogen container suitable for portable electronics equipment

Mass of empty container	0.26 kg
Mass of hydrogen stored	0.0017 kg
Storage efficiency (% mass H ₂)	0.65%
Specific energy	0.26 kWh kg ⁻¹
Volume of tank (approx.)	0.06 l
Mass of H ₂ per litre	0.028 kg l ⁻¹

holder for applications such as portable electronics equipment, manufactured by GfE Metalle und Materialien GMBH of Germany, and shown in Figure 6.5. The volumetric measure, mass of hydrogen per litre, is nearly as good as for LH₂, and the gravimetric measure is not a great deal worse than for compressed gas and very much the same as for a small compressed cylinder. Larger systems have very similar performance.

One of the main advantages of this method is its safety. The hydrogen is not stored at a significant pressure, and so cannot rapidly and dangerously discharge. Indeed, if the valve is damaged or there is a leak in the system, the temperature of the container will fall, which will inhibit the release of the gas. The low pressure greatly simplifies the design of the fuel supply system. It thus has great promise for a very wide range of applications where small quantities of hydrogen are stored. It is also particularly suited to applications where weight is not a problem, but space is.

The disadvantages are particularly noticeable where larger quantities of hydrogen are to be stored, for example in vehicles! The specific energy is poor. Also, the problem of the heating during filling and cooling during release of hydrogen becomes more acute. Large systems have been tried for vehicles, and a typical refill time is about 1 hour for an approximately 5 kg tank. The other major disadvantage is that usually very high-purity hydrogen must be used, otherwise the metals become contaminated, as they react irreversibly with the impurities.

6.5.6 Carbon Nanofibres

In 1998 a paper was published on the absorption of hydrogen in carbon nanofibres (Chambers *et al.*, 1998). The authors presented results suggesting that these materials could absorb in excess of 67% hydrogen by weight, a storage capacity far in excess of any of the others we have described so far. This set many other workers on the same trail. However, it would be fair to say that no one has been able to repeat this type of performance, and methods by which errors could be made in the measurements have been suggested. Nevertheless, other workers have shown fairly impressive storage capability with carbon nanofibres, and this is certainly one to watch for the future – see Chapter 8 of Larminie and Dicks (2003).

6.5.7 Storage Methods Compared

Table 6.5 gives the range of gravimetric, volumetric hydrogen storage and the energy efficiency of storage measures for the systems described above that are broadly available

Table 6.5 Data for comparing methods of storing hydrogen fuel

Method	Gravimetric storage efficiency, % mass hydrogen	Volumetric mass (in kg) of hydrogen per litre	Energy efficiency of storage (energy in stored H ₂)/(energy in H ₂ + energy to store H ₂)
Pressurised gas	0.7–3.0	0.015	0.9 at 200 bar
Reversible metal hydride	0.65	0.028	–
Cryogenic liquid	14.2	0.040	0.75 for large systems

now. Obviously these figures cannot be used in isolation – they do not include cost, for example. Safety aspects do not appear in this table either. The cryogenic storage method has the best figures.

The storage efficiency of compressing hydrogen to 200 bar is at best around 90%. The efficiency of liquefying hydrogen is typically 45% for small systems and 75% for larger systems.

6.6 Hydrogen Storage II – Chemical Methods

6.6.1 Introduction

None of the methods for storing hydrogen outlined in Section 6.5 is entirely satisfactory. Other approaches that are being developed rely on the use of chemical ‘hydrogen carriers’. These could also be described as ‘human-made fuels’. There are many compounds that can be manufactured that hold, for their mass, quite large quantities of hydrogen. To be useful these compounds must pass three tests:

1. It must be possible to make these compounds give up their hydrogen very easily, otherwise there is no advantage over using a reformed fuel in one of the ways already outlined in Section 6.2.
2. The manufacturing process must be simple and use little energy – in other words, the energy and financial costs of putting the hydrogen into the compound must be low.
3. They must be safe to handle.

A large number of chemicals that show promise have been suggested or tried. Some of these, together with their key properties, are listed in Table 6.6. Some of them do not warrant a great deal of consideration, as they easily fail one or more of the three tests above. Hydrazine is a good example. It passes the first test very well, and it has been used in demonstration fuel cells with some success. However, hydrazine is both highly toxic and very energy intensive to manufacture, and so fails the second and third tests. Nevertheless, several of the compounds of Table 6.6 are being considered for practical applications, and will be described in more detail here.

Table 6.6 Liquids that might be used locally to store hydrogen gas for fuel cells

Name	Formula	Percentage H ₂	Density (kg l ⁻¹)	Vol. (l) to store 1 kg H ₂	Notes
Liquid H ₂	H ₂	100	0.07	14	Cold, -252 °C
Ammonia	NH ₃	17.8	0.67	8.5	Toxic, 100 ppm
Liquid methane	CH ₄	25.1	0.415	9.6	Cold, -175 °C
Methanol	CH ₃ OH	12.5	0.79	10	-
Ethanol	C ₂ H ₅ OH	13.0	0.79	9.7	-
Hydrazine	N ₂ H ₄	12.6	1.01	7.8	Highly toxic
30% sodium borohydride solution	NaBH ₄ + H ₂ O	6.3	1.06	15	Expensive, but works well

6.6.2 Methanol

Methanol is the ‘human-made’ carrier of hydrogen that is attracting the most interest among fuel cell developers. As we saw in Section 6.3, methanol can be reformed to hydrogen by steam reforming, according to the following reaction:



The equipment is much more straightforward, though the process is not so efficient, if the partial oxidation route is used, for which the reaction is



The former would yield 0.188 kg of hydrogen for each kilogram of methanol, the latter 0.125 kg of hydrogen for each kilogram of methanol. We have also seen in Section 6.3 that *autothermal* reformers use a combination of both these reactions, and this attractive alternative would provide a yield somewhere between these two figures. The key point is that whatever reformation reaction is used (6.9 or 6.10) the reaction takes place at temperatures of around 250 °C, which is far less than those needed for the reformation of gasoline, as described in Section 6.3 (reaction 6.3 or 6.6). Also, the amount of carbon monoxide produced is far less, which means that far less chemical processing is needed to remove it. All that is needed is one of the four carbon monoxide clean-up systems outlined in Section 6.3.4.

Leading developers of methanol reforming for vehicles at present are Excellis Fuel Cell Engines (DaimlerChrysler), General Motors, Honda, International Fuel Cells, Mitsubishi, Nissan, Toyota and Johnson Matthey. Most are using steam reforming although some organisations are also working on partial oxidation. DaimlerChrysler developed a methanol processor for the Necar 3 experimental vehicle. This was demonstrated in September 1997 as the world’s first methanol-fuelled fuel cell car. It was used in conjunction with a Ballard 50 kW fuel cell stack. Characteristics of the methanol processor are given in Table 6.7.

Table 6.7 Characteristics of the methanol processor for Nekar 3 (Kalhammer *et al.*, 1998)

Maximum unit size	50 kW _e
Power density	1.1 kW _e l ⁻¹ (reformer = 20 l, combustor = 5 l, CO selective oxidiser = 20 l)
Specific power	0.44 kW _e kg ⁻¹ (reformer = 34 kg, combustor = 20 kg, CO sel. oxidiser = 40 kg)
Energy efficiency	Not determined
Methanol conversion	98–100%
Efficiency	–
Turn-down ratio	20 to 1
Transient response	<2 s

Since the Nekar3 demonstration, DaimlerChrysler and Excellsis have been working with BASF to develop a more advanced catalytic reformer system for their vehicles. In November 2000 DaimlerChrysler launched the Nekar5 which, together with a Jeep Commander vehicle, represents the state of the art in methanol fuel cell vehicles. The fuel cell drive system has been shrunk to such an extent that it presently requires no more space than a conventional drive system. The Nekar 5 therefore has the full complement of seats and interior space as a conventional gasoline-fuelled IC engine car. The car is based on the A-Class Mercedes design and the methanol reformer is under the passenger compartment, as illustrated in Figure 6.6. The Nekar 5 uses a Ballard 75 kW Mk 9 stack giving an impressive top speed of over 150 kph.

However, whatever reformer is used, full utilisation is not possible – it never is with gas mixtures containing carbon dioxide, as there must still be some hydrogen in the exit

**Figure 6.6** Packaging of the Nekar 5 methanol fuel processor

Table 6.8 Speculative data for a hydrogen source, storing 40 l (32 kg) of methanol

Mass of reformer and tank	64 kg
Mass of hydrogen stored ^a	4.4 kg
Storage efficiency (% mass H ₂)	6.9%
Specific energy	5.5 kWh kg ⁻¹
Volume of tank + reformer	0.08 m ³
Mass of H ₂ per litre	0.055 kg l ⁻¹

^aAssuming 75% conversion of available H₂ to usable H₂.

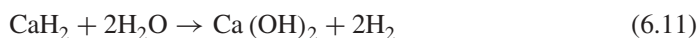
gas, as explained in Section 6.3.1. Also, in the case of steam reforming, some of the product hydrogen is needed to provide energy for the reforming reaction. If we assume that the hydrogen utilisation can be 75%, then we can obtain 0.14 kg of hydrogen for each kilogram of methanol. We can speculate that a 40 l tank of methanol might be used, with a reformer of about the same size and weight as the tank. Such a system should be possible in the reasonably near term, and would give the figures in Table 6.8.

The potential figures show why methanol systems are looked on with such favour, and why they are receiving a great deal of attention for systems of power above about 10 W right through to tens of kilowatts.

We should note that *ethanol*, according to the figures in Table 6.6, should be just as promising as methanol as a hydrogen carrier. Its main disadvantage is that the equivalent reformation reactions of reactions 6.9 and 6.10 do not proceed nearly so readily, making the reformer markedly larger, more expensive, less efficient and more difficult to control. Ethanol is also usually somewhat more expensive. All these disadvantages more than counter the very slightly higher hydrogen content.

6.6.3 Alkali Metal Hydrides

An alternative to the reversible metal hydrides is alkali metal hydrides which react with water to release hydrogen and produce a metal hydroxide. Bossel (1999) has described a system using calcium hydride which reacts with water to produce calcium hydroxide and release hydrogen:



It could be said that the hydrogen is being released from the water by the hydride.

Another method that is used commercially, under the trade name ‘Powerballs’, is based on sodium hydride. These are supplied in the form of polyethylene-coated spheres of about 3 cm diameter. They are stored underwater, and cut in half when required to produce hydrogen. An integral unit holds the water, product sodium hydroxide and a microprocessor-controlled cutting mechanism that operates to ensure a continuous supply of hydrogen. In this case the reaction is



This is a very simple way of producing hydrogen, and its energy density and specific energy can be as good or better than the other methods we have considered so far. Sodium is an abundant element, and so sodium hydride is not expensive. The main problems with these methods are:

- The need to dispose of a corrosive and unpleasant mixture of hydroxide and water. In theory, this could be recycled to produce fresh hydride, but the logistics of this would be difficult.
- The fact that the hydroxide tends to attract and bind water molecules, which means that the volumes of water required tend to be considerably greater than reactions 6.11 and 6.12 would imply.
- The energy required to manufacture and transport the hydride is greater than that released in the fuel cell.

A further point is that the method does not stand very good comparison with metal–air batteries. If the user is prepared to use quantities of water, and is prepared to dispose of water/metal hydroxide mixtures, then systems such as the aluminium–air or magnesium–air battery are preferable. With a saltwater electrolyte, an aluminium–air battery can operate at 0.8 V at quite a high current density, producing three electrons for each aluminium atom. The electrode system is much cheaper and simpler than a fuel cell.

Nevertheless, the method compares quite well with the other systems in several respects. The figures in Table 6.9 are calculated for a self-contained system capable of producing 1 kg of hydrogen, using the sodium hydride system. The equipment for containing the water and gas, and the cutting and control mechanism, is assumed to weigh 5 kg. There is three times as much water as reaction 6.12 would imply is needed.

The storage efficiency compares well with other systems. This method may well have some niche applications where the disposal of the hydroxide is not a problem, though these are liable to be limited.

6.6.4 Sodium Borohydride

A good deal of interest has been shown in the use of sodium tetrahydridoborate, or sodium borohydride as it is usually called, as a chemical hydrogen carrier. This reacts with water to form hydrogen according to the reaction



Table 6.9 Figures for a self-contained system producing 1 kg of hydrogen using water and sodium hydride

Mass of container and all materials	45 kg
Mass of hydrogen stored	1.0 kg
Storage efficiency (% mass H ₂)	2.2%
Specific energy	0.87 kWh kg ⁻¹
Volume of tank (approximately)	50 l
Mass of H ₂ per litre	0.020 kg l ⁻¹

This reaction does not normally proceed spontaneously, and solutions of NaBH_4 in water are quite stable. Some form of catalyst is usually needed. The result is one of the great advantages of this system – it is highly controllable. Millennium Cell Corp. in the USA has been actively promoting this system and has built demonstration vehicles running on both fuel cells and IC engines using hydrogen made in this way. Companies in Europe, notably NovArs GmbH in Germany (Koschany, 2001), have also made smaller demonstrators. Notable features of reaction 6.13 are:

- It is exothermic, at the rate of 54.5 kJ per mole of hydrogen.
- Hydrogen is the only gas produced; it is not diluted with carbon dioxide.
- If the system is warm, then water vapour will be mixed with the hydrogen, which is highly desirable for PEMFC systems.

Although rather overlooked in recent years, NaBH_4 has been known as a viable hydrogen generator since 1943. The compound was discovered by the Nobel laureate Herbert C. Brown, and the story is full of interest and charm, but is well told by Professor Brown himself elsewhere (Brown, 1992). Suffice to say that shortly before the end of the Second World War, plans were well advanced to bulk-manufacture the compound for use in hydrogen generators by the US Army Signals Corps, when peace rendered this unnecessary. However, in the following years many other uses of sodium borohydride, notably in the paper processing industries, were discovered, and it is produced at the rate of about 5000 tonnes per year (*Kirk-Othmer Encyclopedia of Chemical Technology*), mostly using Brown's method, by Morton International (merged with Rohm and Haas in 1999).

If mixed with a suitable catalyst, sodium borohydride can be used in solid form, and water added to make hydrogen. The disadvantage of this method is that the material to be transported is a flammable solid, which spontaneously gives off hydrogen gas if it comes into contact with water. This is obviously a safety hazard. It is possible to purchase sodium borohydride mixed with 7% cobalt chloride for this purpose. However, this is not the most practical way to use the compound.

Current work centres on the use of solutions. This has several advantages. Firstly the hydrogen source becomes a single liquid – no separate water supply is needed. Secondly this liquid is not flammable, and only mildly corrosive, unlike the solid form. The hydrogen-releasing reaction of reaction 6.13 is made to happen by bringing the solution into contact with a suitable catalyst. Removing the catalyst stops the reaction. The gas generation is thus very easily controlled – a major advantage in fuel cell applications.

The maximum practical solution strength used is about 30%. Higher concentrations are possible, but take too long to prepare and are subject to loss of solid at lower temperatures. The solution is made alkaline by the addition of about 3% sodium hydroxide, otherwise the hydrogen evolution occurs spontaneously. The 30% solution is quite thick, and so weaker solutions are sometimes used, even though their effectiveness as a hydrogen carrier is worse. One litre of a 30% solution will give 67 g of hydrogen, which equates to about 800 NL. This is a very good volumetric storage efficiency.

Generators using these solutions can take several forms. The principle is that to generate hydrogen the solution is brought into contact with a suitable catalyst, and that generation ceases when the solution is removed from the catalyst. Suitable catalysts include platinum and ruthenium, but other less expensive materials are effective, including iron oxide. Fuel cell electrodes make very good reactors for this type of generator.

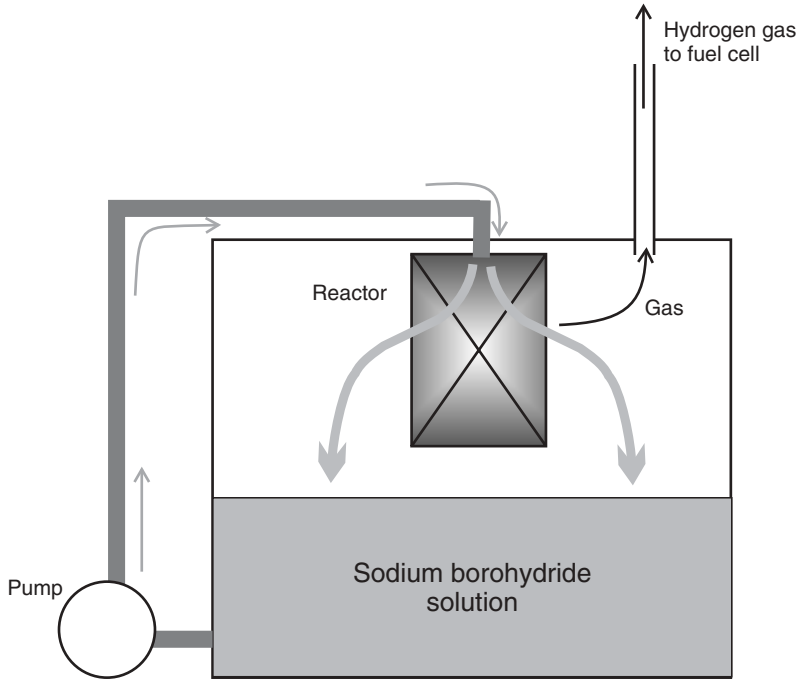


Figure 6.7 Example reactor for releasing hydrogen from a solution of sodium borohydride in water, stabilised with sodium hydroxide. The rate of production of hydrogen is controlled by varying the rate at which the solution is pumped over the reactor

A practical sodium borohydride system is shown in Figure 6.7. The solution is pumped over the reactor, releasing hydrogen. The motor driving the pump is turned on and off by a simple controller that senses the pressure of the hydrogen, and which turns it on when more is required. The solution is forced through the reactor, and so fresh solution is continually brought in contact with the catalyst. The rate of production is simply controlled by the duty cycle of the pump. The reaction takes place at room temperature, and the whole system is extremely simple when compared with any of the other generators that have been outlined in this section.

However, when the solution is weak, the reaction rate will be much slower, and the system will behave differently. It is likely that it will not be practical to obtain highly efficient solution usage. Also, the solution cannot be renewed at the user's convenience – it must be completely replaced when the sodium borohydride has been used up, and at no other time.

Another method that is used is that of the Hydrogen on Demand system which was promoted by Millennium Cell. This uses a single-pass catalyst, rather than the recirculation system of Figure 6.7. A major advantage of this is that the tank of fresh solution can be topped up at any time. A disadvantage is that two tanks are needed – the second one for the spent solution that has passed over the catalyst.

In terms of the general figure of merit 'volume required to produce 1 kg of hydrogen', the 30% NaBH_4 solution is the worst of the liquid carriers listed in Table 6.6. However,

it is competitive and is only very slightly worse than pure liquid hydrogen. However, it has many advantages over the other technologies:

- It is arguably the safest of all the liquids to transport.
- Apart from cryogenic hydrogen it is the only liquid that gives pure hydrogen as the product. *This is very important*, as it means it is the only one where the product gas can be 100% utilised within the fuel cell.
- The reactor needed to release the hydrogen requires no energy, and can operate at ambient temperature and pressure.
- The rate of production of hydrogen can be simply controlled.
- The reactor needed to promote the hydrogen production reaction is very simple – far simpler than that needed for any of the other liquids.
- If desired, the product hydrogen gas can contain large quantities of water vapour, which is highly desirable for PEMFCs.

In order to compare a complete system, and produce comparative figures for gravimetric and volumetric storage efficiency, we need to speculate what a complete hydrogen generation system would be like. Systems have been built where the mass of the unit is about the same as the mass of the solution stored, and about twice the volume of solution held. So, a system that holds 1 l of solution has a volume of about 2 l, and weighs about 2 kg. Such a system would yield the figures given in Table 6.10.

These figures are very competitive with all other systems. So what are the disadvantages? There are three main problems, the second two being related. The first is the problem of disposing of the borate solution. This is not unduly difficult, as it is not a hazardous substance. However, the other disadvantages are far more severe. The first is the cost. Sodium borohydride is an expensive compound. By simple calculation and reference to catalogues it can be shown that the cost of producing hydrogen this way is about \$630 per kilogram.² This is over 100 times more expensive than using an electrolyser driven by grid-supplied electricity (see Larminie, 2002). At this sort of cost the system is not at all viable.

Linked to this problem of cost is the energy required to manufacture sodium borohydride. Using current methods this far exceeds the requirements of compounds such as methanol. Currently sodium borohydride is made from borax ($\text{NaO} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$), a

Table 6.10 Speculative data for a hydrogen source, storing 1.0 l of 30% NaBH_4 , 3% NaOH and 67% H_2O solution

Mass of reformer, tank and solution	2.0 kg
Mass of hydrogen stored	0.067 kg
Storage efficiency (% mass H_2)	3.35%
Specific energy	1.34 kWh kg^{-1}
Volume of system (approximately)	2.0 l
Mass of H_2 per litre	0.036 kg l^{-1}

² 2003 prices.

Table 6.11 Key thermodynamic data for sodium borohydride and borate

	NaBH ₄	NaBO ₂
Molar enthalpy of formation (kJ mol ⁻¹)	-189	-977

naturally occurring mineral with many uses that is mined in large quantities, and methanol. The aim is that the sodium metaborate produced by the hydrolysis reaction (6.13) is recycled back to sodium borohydride. Table 6.11 gives the molar enthalpies of formation of the key compounds. It can be seen that such recycling will be a formidable challenge, requiring at least 788 kJ mol⁻¹. However, the ‘prize’ is 4 mol of hydrogen, so that is at least 197 kJ mol⁻¹, which is not quite so daunting. Nevertheless, there are many problems to be overcome before such recycling is viable.

The companies which are hoping to commercialise this process are working hard on this problem of production cost – finance and energy. If they succeed there will be a useful hydrogen carrier, but until the costs come down by a factor of at least 10 then this method is only suitable for special niche applications.

6.6.5 Ammonia

Ammonia is a colourless gas with a pungent choking smell that is easy to recognise. It is highly toxic. The molecular formula is NH₃, which immediately indicates its potential as a hydrogen carrier. It has many uses in the chemical industry, the most important being in the manufacture of fertiliser, which accounts for about 80% of the use of ammonia. It is also used in the manufacture of explosives. Ammonia is produced in huge quantities. The annual production is estimated at about 100 million tonnes, of which a little over 16 million is produced in the USA.³

Ammonia liquefies at -33 °C, not an unduly low temperature, and can be kept in liquid form at normal temperature under its own vapour pressure of about 8 bar – not an unduly high pressure. Bulk ammonia is normally transported and stored in this form. However, it also readily dissolves in water – in fact it is the most water-soluble of all gases. The solution (ammonium hydroxide) is strongly alkaline, and is sometimes known as ‘ammonia water’ or ‘ammonia liquor’. Some workers have built hydrogen generators using this as the form of ammonia supplied, but this negates the main advantage of ammonia, which is its high ‘hydrogen density’, as well as adding complexity to the process.

Liquid ammonia is one of the most compact ways of storing hydrogen. In terms of volume needed to store 1 kg of hydrogen, it is better than almost all competing materials – see Table 6.6. Counter-intuitively it is approximately 1.7 times as effective as liquid hydrogen. (This is because, even in liquid form, hydrogen molecules are very widely spaced, and LH₂ has a very low density.)

Table 6.6 shows ammonia to be the best liquid carrier, in terms of space to store 1 kg of hydrogen – apart from hydrazine, which is so toxic and carcinogenic that it is

³ Information provided by the Louisiana Ammonia Producers Association, www.lammonia.com.

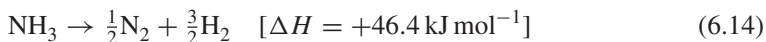
definitely not a candidate for regular use. However, the margin between the leading candidates is not very large. The figures ignore the large size of container that would be needed, especially in the case of ammonia, liquid methane and LH_2 , though not for the key rival compound methanol.

Two other features of ammonia lie behind the interest in using it as a hydrogen carrier. The first is that large stockpiles are usually available, due to the seasonal nature of fertiliser use. The second is that ammonia prices are sometimes somewhat depressed due to an excess of supply over demand. However, when the details of the manufacture of ammonia, and its conversion back to hydrogen, are considered, it becomes much less attractive.

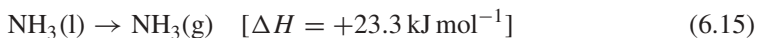
Using ammonia as a hydrogen carrier involves the manufacture of the compound from natural gas and atmospheric nitrogen, the compression of the product gas into liquid form, and then, at the point of use, the dissociation of the ammonia back into nitrogen and hydrogen.

The production of ammonia involves the steam reformation of methane (natural gas), as outlined in Section 6.3. The reaction has to take place at high temperature, and the resulting hydrogen has to be compressed to very high pressure (typically 100 bar) to react with nitrogen in the Haber process. According to the Louisiana Ammonia Producers Association, which makes about 40% of the ammonia produced in the USA, the efficiency of this process is about 60%. By this the Association means that 60% of the gas used goes to provide hydrogen, and 40% is used to provide energy for the process. This must be considered a ‘best case’ figure, since there will no doubt be considerable use of electrical energy to drive pumps and compressors that is not considered here. The process is inherently very similar to methanol production – hydrogen is made from fuel, and is then reacted with another gas. In this case it is nitrogen instead of carbon dioxide. The process efficiencies and costs are probably similar.

The recovery of hydrogen from ammonia involves the simple dissociation reaction



For this reaction to occur at a useful rate the ammonia has to be heated to between 600 and 800 °C, and passed over a catalyst. Higher temperatures of about 900 °C are needed if the output from the converter is to have remnant ammonia levels down to the parts per million level. On the other hand the catalysts need not be expensive: iron, copper, cobalt and nickel are among many materials that work well. The reaction is endothermic, as shown. However, this is not the only energy input required. The liquid ammonia absorbs large amounts of energy as it vaporises into a gas, which is why it is still quite extensively used as a refrigerant:



Once a gas at normal temperature, it then has to be heated, because the dissociation reaction only takes place satisfactorily at temperatures of around 800–900 °C. For simplicity we will assume a temperature rise of 800 °C. The molar specific heat of ammonia is $36.4 \text{ J mol}^{-1} \text{ kg}^{-1}$, so

$$\Delta H = 800 \times 36.4 = 29.1 \text{ kJ mol}^{-1}$$

This process results in the production of 1.5 mol of hydrogen, for which the molar enthalpy of formation (HHV) is $-285.84 \text{ kJ mol}^{-1}$. The best possible efficiency of this stage of the process is thus

$$\frac{(285.84 \times 1.5) - (23.3 + 29.1 + 46.4)}{285.84 \times 1.5} = 0.77 = 77\%$$

This should be considered an upper limit of efficiency, as we have not considered the fact that the reformation process will involve heat losses to the surroundings. However, systems should be able to get quite close to this figure, since there is scope for using heat recovery, as the product gases would need to be cooled to about 80°C before entering the fuel cell. The vaporisation might also take place at below ambient temperature, allowing some heat to be taken from the surroundings.

The corrosive nature of ammonia and ammonium hydroxide is another major problem. Water is bound to be present in a fuel cell. Any traces of ammonia left in the hydrogen and nitrogen product gas stream will dissolve in this water, and thus form an alkali (ammonium hydroxide) inside the cell. In small quantities, in an alkaline electrolyte fuel cell, this is tolerable. However, in the PEMFC it would be fatal. This point is admitted by some proponents of ammonia, and is used by them as an advantage for alkaline fuel cells (e.g. Kordesch *et al.*, 1999). Hydrogen from other hydrogen carriers such as methanol and methane also contains poisons, notably carbon monoxide. However, these can be removed and do not permanently harm the cell – they just temporarily degrade performance. Ammonia, on the other hand, will do permanent damage, and this damage will steadily get worse and worse.

Ammonia as a hydrogen carrier can well be compared with methanol. If it were, the following points would be made:

- The production methods and costs are similar.
- The product hydrogen per litre of carrier is slightly better.
- Ammonia is far harder to store, handle and transport.
- Ammonia is more dangerous and toxic.
- The process of extracting the hydrogen is more complex.
- The reformer operates at very high temperatures, making integration into small fuel cell systems much more difficult than for methanol.
- The product gas is difficult to use with any type of fuel cell other than alkaline.

The conclusion must be that the use of ammonia as a hydrogen carrier is going to be confined to only the most unusual circumstances.

6.6.6 Storage Methods Compared

We have looked at a range of hydrogen storage methods. In Section 6.3 we looked at fairly simply ‘hydrogen in, hydrogen out’ systems. In Section 6.5 we looked at some more complex systems involving the use of hydrogen-rich chemicals that can be used as carriers.

None of the methods is without major problems. Table 6.12 compares the systems that are currently feasible in relation to gravimetric and volumetric effectiveness. Together with the summary comments, this should enable the designer to choose the least

Table 6.12 Data for comparing methods of storing hydrogen fuel. The figures include the associated equipment, for example tanks for liquid hydrogen, or reformers for methanol

Method	Gravimetric storage efficiency, % mass H ₂	Volumetric mass (in kg) of H ₂ per litre	Comments
High pressure in cylinders	0.7–3.0	0.015	‘Cheap and cheerful’, widely used
Metal hydride	0.65	0.028	Suitable for small systems
Cryogenic liquid	14.2	0.040	Widely used for bulk storage
Methanol	6.9	0.055	Low-cost chemical. Potentially useful in a wide range of systems
Sodium hydride pellets	2.2	0.02	Problem of disposing of spent solution
NaBH ₄ solution in water	3.35	0.036	Very expensive to run

difficult alternative. It is worth noting that the method with the worst figures (storage in high-pressure cylinders) is actually the most widely used. This is because it is so simple and straightforward. The figures also show why methanol is such a promising candidate for the future.

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