Extension 27: The Hydrogen Economy

1. Prerequisites

The ideas which form the background to this unit are listed in the following table:

Topic	Book page
Energy density	228
Gas compression (Boyle's Law)	160
Global warming	410

The background

About 85% of the world's primary energy comes from fossil fuels. Nuclear power (8.5%) and hydroelectric power (6.5%) make the next largest contributions, with other renewable energy sources making up less than one per cent.

Concern about Global Warming and CO_2 emissions, the stocks of fossil fuels and the security of supply has 'concentrated minds' over alternative energy sources and different ways of powering road vehicles. The ideal characteristics of a vehicle fuel include the following. It should:

1. Provide a lot of energy per gram.
2. Be cheap to make or extract.
3. Not pollute the atmosphere or poison people when it is burned.
4. Have a small 'carbon fingerprint'.
5. Occupy a small volume per g of fuel so that it is easily and cheaply transported.

No one fuel is ideal! One suggestion is that countries move towards a 'Hydrogen Economy' in which hydrogen acts as a carrier of energy and where hydrogen-powered cars may have displaced diesel or petrol cars. Molecular hydrogen (H_2) does not occur naturally on Earth and energy is expended in extracting H_2. It follows that hydrogen is not a primary fuel (like coal or natural gas) and is better referred to as an 'energy carrier' or 'energy vector'. As we discuss in more detail below, getting energy from H_2 is relatively environmentally friendly at the point of combustion, although (like many gaseous fuels) it is not especially easy to handle and store.

This extension unit focuses on the possible large-scale uses of hydrogen as a car fuel. In studying this topic, we will discover that the scaling up of hydrogen technology poses many challenges. At the heart of the matter is chemistry: how do we use, make and store hydrogen?

2. Energy density of fuels

The energy value of a fuel is the amount of heat produced when 1 g of the fuel is completely burned. The units of energy value are kJ g^{-1}. Table 1 shows the energy values of some fuels.

Table 1 Properties of selected fuels

Fuel	*State at 25°C*	*Volume of 1 g of fuel at 25°C/cm^3*	*Energy value/kJ g^{-1}*	*Energy density/ at kJ cm^{-3} at 25°C*
Methane CH_4	gas	1400	56	0.040
Octane C_8H_{18}	liquid	1.3	48	37
Methanol CH_3OH	liquid	1.3	23	18
Hydrogen H_2	gas	11000	142	0.013

EXERCISE 27A

Use Table 1 to answer the following questions.

(i) Which of the listed fuels:

(a) Produces the most energy per gram of fuel?

(b) Produces the least energy per cm^3 of fuel?

(ii) Why do cars running on natural gas (methane) need larger fuel tanks than petrol-driven cars? (Petrol has a typical energy density of 34 kJ g^{-1}, close to that of octane.)

(iii) What volume of hydrogen gas gives out the same energy when burned as 1cm3 of octane?

(iv) How could you increase the energy density of hydrogen?

Answer

(i) **(a)** Hydrogen, and;

(b) Hydrogen.

(ii) Methane is a gas, which occupies a greater volume than the same mass of petrol at room temperature.

(iii) (37/0.013) × 1cm^3 = 2846 cm^3.

(iv) Compress the hydrogen.

Petrol possesses a high energy density because it is a liquid. However, whereas the energy value, in kJ g^{-1}, of a named fuel cannot be changed, the volume of a gaseous fuel can be reduced by compression or even liquefaction, so changing the energy density of the fuel. Experiments show that 1.0 g of liquid hydrogen at its boiling point (-252 °C) occupies 14 cm^3, increasing its energy density to a respectable 10.1 kJ cm^{-3}. Even so, the energy density of liquefied H_2 is only 40% of that of petrol so you need to carry 2.5 times the volume of $H_2(l)$ in a vehicle to equal the energy output of one volume of petrol. Another way of storing hydrogen in cars, using a hydride battery, is explored in section 5.

3. Using hydrogen fuel to power a car

When hydrogen is burned in oxygen a flame is produced:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

and water is the only product. This satisfies requirement 3 of our 'Ideal Fuel List' (above), since no CO_2 or particulates are produced and water vapour is non-toxic.

The obvious way to use H_2 would be to burn it in a modified internal combustion engine but it is more efficient to use H_2 to generate electricity as the vehicle moves, using a device called a **fuel cell**. The fuel cell takes the place of the engine in a conventional car. Many companies are carrying out research and development into more efficient and less expensive fuel cells, but much progress has already been made.

A fuel cell uses a chemical reaction to produce electricity not heat and so there is no flame. Unlike an electric battery, a fuel cell can continue to produce electricity if it is continually fed with H_2. The electricity is then used to power an electric motor which drives the vehicle's wheels forward - as it would be in a standard electric car. In other words, a car that uses a hydrogen fuel cell is a special kind of electric car which makes its own electricity by reacting hydrogen in a fuel cell. Therefore, hydrogen cars have the advantage of all electric cars: they have few moving parts and are extremely quiet. Indeed, one of the first observations most people make when travelling in a hydrogen-powered vehicle is that it is difficult to know whether or not 'the engine' is turned on!

The **proton exchange membrane cell** (PEM), Fig 25.2, is well suited to use in hydrogen-powered cars because it operates at relatively low temperatures (below 100 °C). It contains a polymer electrolyte membrane (also – confusingly - abbreviated PEM), However, the platinum catalyst in the cell may become poisoned if the H_2 is impure.

Electrons are produced at the anode of the PEM by the oxidation reaction:

$$2H_2(g) \rightarrow 4H^+(aq) + 4e^- \qquad (1)$$

The reduction reaction at the cathode is:

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

The overall reaction is obtained by adding these equations:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad (3)$$

This confirms that in the fuel cell, hydrogen and oxygen are converted to water.

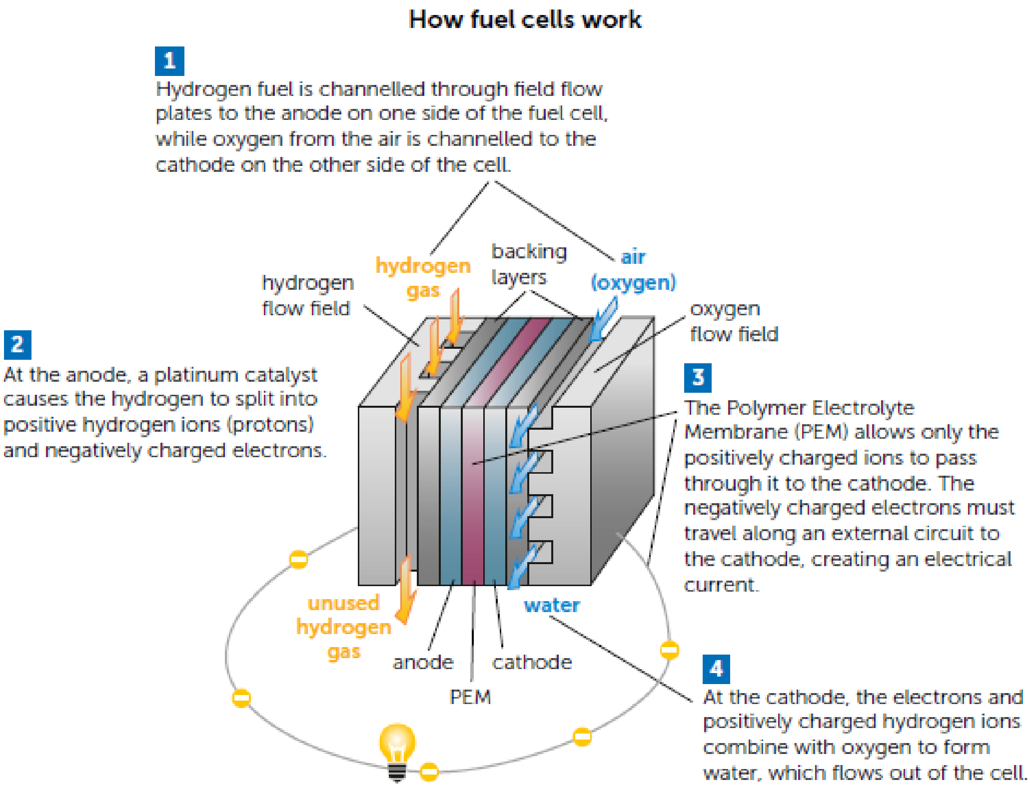

Fig. 27.1 How a PEM Works. The electrons flow from the anode to the cathode

Fig. 27.2 Hydrogen vehicle refuelling area at Baglan Bay, South Wales. The building contains a commercial electrolyser which produces H_2 (see Fig. 25.3(b)) powered by photo-voltaic cells on the building roof. Photograph courtesy of John Maddy, SERC, University of South Wales.

EXERCISE 27B

H_2 has an energy value of 142 kJg^{-1}. In a H_2 powered car:

(a) The hydrogen gas is compressed using pumps and liquefied to H_2(l) at very low temperatures for storage as fuel for the fuel cell; 30 kJ of energy is consumed in producing 1 g of H_2(l).

(b) The hydrogen is used up in a PEM fuel cell with an overall efficiency of 40%.

Calculate the combined percentage efficiency of these processes.

Answer

Of the 142 kJ maximum energy output (realized if 1 g of hydrogen were to be burned in oxygen in a flame), 30 kJ is used up in the liquefaction stage. Of the 112 kJ left, only 40% (44.8 kJ) appears as electricity. The % electricity is therefore (44.8/142) × 100 = 31.5%. This ignores other energy losses in the electric motor and car transmission.

4. Storing the hydrogen

Liquefying hydrogen requires considerable energy expenditure and liquid hydrogen tanks in cars would have to be insulated in order to keep the hydrogen cool. Similarly, the dispensing of liquid H_2 at roadside fuel stations is not as straightforward. For these reasons, scientists have been experimenting with the storage of gaseous hydrogen in the form of metal hydride 'batteries' which would be stored in the cars in place of the fuel tank. Metal hydrides are compounds formed between hydrogen and a metal e.g. lithium hydride:

$$2Li(s) + H_2(g) \rightarrow 2LiH(s)$$

The idea is that when hydrogen is required by the fuel cell, the hydride is warmed and dissociation occurs:

$$2LiH(s) \rightarrow 2Li(s) + H_2(g)$$

In order for the PEM fuel cell to continue working, the temperature and pressure range at which hydride decomposition occurs must be 1 – 10 atmospheres and 25–120°C. LiH dissociates only at 700 °C and so is unsuitable and the search continues for other candidates. The 2010 US Department of Energy target for such storage systems is that they should be capable of storing not less than 6% by mass of hydrogen: below this it would not be worth using as a hydrogen storage device.

5. Where does the hydrogen come from?

Industrially, the most important way of making H_2 is by stripping hydrogen from water using methane: a chemical reaction called 'steam reforming'. Since the reaction is endothermic a high temperature (1000˚C) is required to produce a high concentration of products:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (4)$$

The gas mixture produced is called 'synthesis gas'. A second (slightly exothermic) reaction is carried out at about 100°C:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (5)$$

Hydrogen may also be made by the electrolysis of acidified water, a process often demonstrated in schools using a Hoffmann Voltameter (Fig 27.3a). Electrolysis it is an energetically demanding process. To produce 1 g of H_2(g):

$$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2} O_2(g)$$

requires about 200 kJ. This exceeds the energy value of hydrogen itself: in other words, the production of 1g of hydrogen by electrolysis uses up more energy than is liberated if 1 g of H_2 is burned in air. One way of achieving a successful hydrogen economy is to make hydrogen from renewable energy e.g. by using photovoltaic (solar) cells or by hydro-electric schemes.

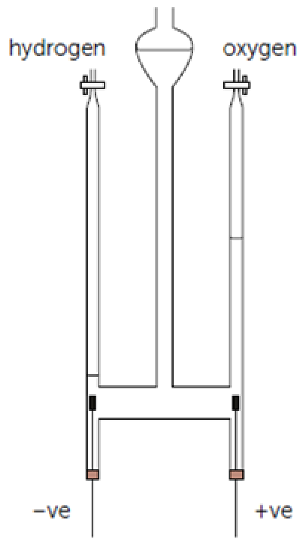

Fig 27.3(a) Hoffmann-Voltameter, with positively and negatively charged platinum electrodes, used to electrolyse acidified water on a small scale in the laboratory.

Fig 27.3(b) Small commercial electrolyser. Photograph courtesy of John Maddy, SERC, University of South Wales.

EXERCISE 27C

Creating a hydrogen economy

What infrastructure would be needed to maintain a vehicular hydrogen economy?

Answer

A large scale national system of (a) H_2 transportation; (b) dispensing stations so that drivers can fill up wherever they travel; and (c) garages equipped to maintain and service H_2-vehicles at reasonable prices etc.

6. The Hydrogen Economy and wider issues relating to fossil fuels

It is likely that there will be greater use of hydrogen as an energy carrier in the future. The attractions of the Hydrogen Economy include a reduction on the dependence on imports of fossil fuels and the potential to significantly reduce greenhouse gas emissions. Initial development of the hydrogen economy is particularly likely in niche geographical markets or countries where renewable energy is relatively abundant, or where there is a strong political will to 'decarbonise transport' e.g. to move away from diesel or petrol powered cars . This alone is a good reason for the study of the science and technology associated with the Hydrogen Economy. However, there are a number of arguments for and against the use of hydrogen as a dominating energy carrier on a large scale across the world, including its use in vehicles.

First, most of the economically viable H_2 produced on a large scale is manufactured using fossil fuels. Hydrogen produced in this way does not solve generic environmental problems (including massive CO_2 emissions) arising from the use of fossil fuels to manufacture, store and transport H_2. For example, why would we use CH_4 (natural gas) to make H_2 (reaction (4) above) when we could burn CH_4 to produce electricity in a power station directly?

On the other hand, against an inevitable long-term trend of increasing fossil fuel prices, there is potential for hydrogen produced from renewable sources to become economically competitive. Among the large number of renewable methods to produce hydrogen there are several promising technologies, including the production of H_2 by bacteria, as well as electrolysis. In addition, the development of economically viable technology to capture CO_2 ('carbon sequestration') from the combustion of fossil fuels may mean that the production of H_2 by fossil fuel routes to hydrogen can be environmentally justified.

Second, less energy is expended in charging electric car batteries directly with electricity than using electricity (or other energy sources) to manufacture, compress, distribute and store H_2. In addition, fuel cells are presently expensive, although they are reducing in cost. According to this argument, standard electric cars are to be preferred over hydrogen-powered electric cars. At its simplest, this is an argument that the fewer stages there are in producing and storing energy, the better, although another possibility is that hybrid cars (using both electrical and fossil fuel energy) rather than 'pure' electric cars will be used in the future.

The relative merits of standard electric cars and hydrogen-powered electric cars have often been debated. Hydrogen-propelled vehicles have longer journey ranges than electric cars, can be significantly lighter and re-fuelling a car with H_2 is quicker than the re-charging of a car battery. On the other hand, it can be claimed that most car journeys are of relatively short duration and electricity has the advantage that it is already widely distributed throughout most countries.

However, many vehicle manufacturers agree that it is spurious to view this as a competition between vehicles powered by electric batteries and vehicles powered by hydrogen. Instead, they should be viewed as complementary developments. Battery electric technology will be suited to small vehicles requiring a limited range. Hydrogen vehicles (whether fuel cell or internal combustion engine) will incorporate much of the technology developed for battery electric vehicles and will be suited to larger vehicles requiring a greater range.

Chemistry will continue to be heavily involved in the future energy economy. Perhaps the biggest challenge of all is not simply about transport but about the sources of all our future energy. It is how to produce renewable energy (which does not contribute to global warming) on a very much larger scale than at present. This is difficult for many reasons. For example, despite recent increases in prices, fossil fuels remain relatively cheap and are also relatively abundant (particularly coal). This makes the wide-scale development of renewable energy uneconomic without government intervention. Where we do have to use fossil fuels in the future, it will be important to be able to store the CO_2 produced from fossil fuels on a massive scale. If renewable energy sources are more fully exploited then energy will be available for many purposes, including the widespread use of hydrogen powered vehicles.

Fig. 27.4 Aspects of the H_2 economy.