

# Hydrogen Fuel Cell Vehicles and Hydrogen Storage Techniques

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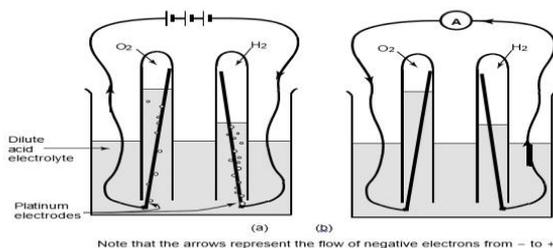
**Abstract-** At the present day, Hydrogen is an especially attractive transportation fuel. It is the least polluting fuel available, and can be produced anywhere there is water and a clean source of electricity. A fuel cycle in which hydrogen is produced by solar-electrolysis of water, or by gasification of renewably grown biomass, and then used in a fuel-cell powered electric-motor vehicle (FCEV), would produce little or no local, regional, or global pollution. Hydrogen FCEVs would combine the best features of battery-powered electric vehicles (BPEVs) -- zero emissions, high efficiency, quiet operation and long life -- with the long range and fast refuelling time of internal-combustion-engine vehicles (ICEVs). If fuel-cell technology develops as hoped, then hydrogen FCEVs will be a significant advance over both hydrogen ICEVs and solar BPEVs: they will be cleaner and more efficient than hydrogen ICEVs, have a much shorter refuelling time than BPEVs, and have a lower lifecycle cost than both. Solar-hydrogen fuel-cell vehicles would be general-purpose zero-emission vehicles, and could be an important component of strategy for reducing dependence on imported oil, mitigating global warming, and improving urban air quality, at an acceptable cost. The only problem behind this technology is storage of hydrogen in on-board Vehicles.

**Keyword:** Hydrogen fuel cell, Connecting cells, Gas supply and cooling, Fuel cell types, Hydrogen storage.

## INTRODUCTION

### A. Hydrogen Fuel Cells – Basic Principles

The basic operation of the hydrogen fuel cell is extremely simple. The first demonstration of a fuel cell was shown in 1839, using an experiment along the lines of that shown, water is being electrolysed into hydrogen and oxygen by passing an electric current through it, the power supply has been replaced with an ammeter, and a small current is flowing.



Note that the arrows represent the flow of negative electrons from - to +.

**figure 1 (a) The electrolysis of water. The water is separated into hydrogen and oxygen by the passage of an electric current. (b) A small current flows. The oxygen and hydrogen are recombining.**

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The electrolysis is being reversed – the hydrogen and oxygen are recombining, and an electric current is being produced. Another way of looking at the fuel cell is to say that the hydrogen fuel is being ‘burnt or combusted in the simple reaction  $2H_2 + O_2 \rightarrow 2H_2O$ .....(1)

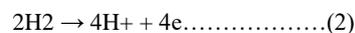
However, instead of heat energy being liberated, electrical energy is produced.

The experiment makes a reasonable demonstration of the basic principle of the fuel cell, but the currents produced are very small. The main reasons for the small current are

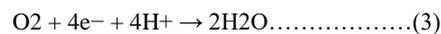
- The low ‘contact area’ between the gas, the electrode, and the electrolyte – basically just a small ring where the electrode emerges from the electrolyte.
- The large distance between the electrodes – the electrolyte resists the flow of electric current.

To overcome these problems, the electrodes are usually made flat, with a thin layer of electrolyte. The structure of the electrode is porous so that both the electrolyte from one side and the gas from the other can penetrate it. This is to give the maximum possible contact between the electrode, the electrolyte, and the gas. However, to understand how the reaction between hydrogen and oxygen produces an electric current, and where the electrons come from, we need to consider the separate reactions taking place at each electrode. These important details vary for different types of fuel cells, but if we start with a cell based around an acid electrolyte, as used by Grove, we shall start with the simplest and still the most common type.

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

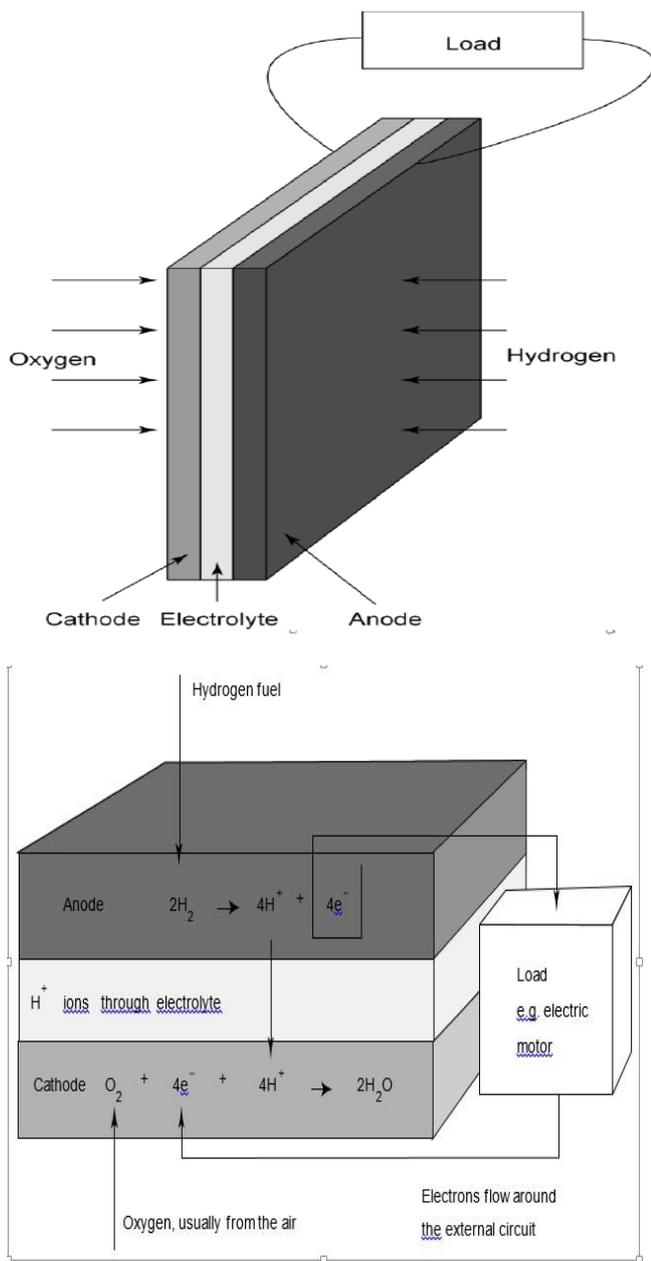


This reaction releases energy. At the cathode, oxygen reacts with electrons taken from the electrode, and  $H^+$  ions from the electrolyte, to form water.



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. These materials are called *proton exchange membranes*, as an  $H^+$  ion is also a proton. Comparing equations 2 and 3 we can see that two hydrogen molecules will be needed for each oxygen molecule if the system is to be kept in balance. It should be noted that the electrolyte must only allow  $H^+$  ions to pass through it, and not electrons. Otherwise, the electrons would go through the electrolyte, not a round the external circuit, and all would be lost.

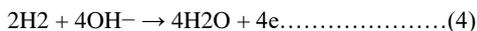




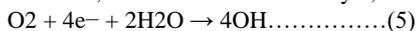
**Figure 1.2 Electrode reactions and charge flow for an acid electrolyte fuel cell.**

Note that although the negative electrons flow from anode to cathode, the ‘conventional current’ flows from cathode to anode.

In an **alkaline electrolyte fuel cell** the overall reaction is the same, but the reactions at each electrode are different. In an alkali, hydroxyl (OH<sup>-</sup>) ions are available and mobile. At the anode, these react with hydrogen, releasing energy and electrons, and producing water.



At the cathode, oxygen reacts with electrons taken from the electrode, and water in the electrolyte, forming new OH<sup>-</sup> ions.



For these reactions to proceed continuously, the OH<sup>-</sup> ions must be able to pass through the electrolyte, and there must be an electrical circuit for the electrons to go from the anode to the cathode. Also, comparing equations 4 and 5 we see that, as with the acid electrolyte, twice as much as hydrogen is needed as oxygen.

## B. What Limits the Current?

At the anode, hydrogen reacts, releasing energy. However, just because energy is released, it does not mean that the reaction proceeds at an unlimited rate. The reaction has the ‘classical’ energy form, Although energy is released, the ‘activation energy’ must be supplied to get over the ‘energy hill’. If the probability of a molecule having enough energy is low, then the reaction will only proceed slowly. Except at very high temperatures, this is indeed the case for fuel cell reactions.

The three main ways of dealing with the slow reaction rates are

- the use of catalysts,
- raising the temperature,
- 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 equation 4, we see that fuel gas and OH<sup>-</sup> ions from the electrolyte are needed, as well as the necessary activation energy. Furthermore, this ‘coming together’ of H<sub>2</sub> fuel and OH<sup>-</sup> ions must take place on the surface of the electrode, as the electrons produced must be removed.

This reaction, involving fuel or oxygen (usually a gas), with the electrolyte (solid or liquid) and the electrode, is sometimes called the *three phase contact*. The bringing together of these three things is a very important issue in fuel cell design. Clearly, the rate at which the reaction happens will be proportional to the area of the electrode. This is very important. Indeed, electrode area is such a vital issue that the performance of a fuel cell design is often quoted in terms of the current *per cm<sup>2</sup>*.

However, the straightforward area (length × width) is not the only issue. As has already been mentioned, the electrode is made highly porous. This has the effect of greatly increasing the effective surface area. Modern fuel cell electrodes have a microstructure that gives them surface areas that can be hundreds or even thousands of times their straightforward ‘length × width’. The microstructural design and manufacture of a fuel cell electrode is thus a very important issue for practical fuel cells. In addition to these surface area considerations, the electrodes may have to incorporate a catalyst and endure high temperatures in a corrosive environment.

## C. Connecting Cells in Series – the Bipolar Plate

The voltage of a fuel cell is quite small, about 0.7V when drawing a useful current. This means that to produce a useful voltage many cells have to be connected in series. Such a collection of fuel cells in series is known as a ‘stack’. The most obvious way to do this is by simply connecting the edge of each anode to the cathode of the next cell, all along the line, as in Figure 1.7. (For simplicity, this diagram ignores the problem of supplying gas to the electrodes.)

The problem with this method is that the electrons have to flow across the face of the electrode to the current collection point at the edge. The electrodes might be quite good conductors, but if each cell is only operating at about 0.7V, even a small voltage drop is important. Unless the current flows are very low, and the electrode is a particularly good conductor, or very small, this method is not used. A much better method of cell interconnection is to use a ‘bipolar plate’. This makes connections all over the surface of one cathode and the anode of the next cell (hence ‘bipolar’); at the same time, the bipolar plate serves as a means of feeding oxygen to the cathode and fuel gas to the anode. Although a good electrical connection must be made between the two electrodes, the two gas supplies must be strictly separated.

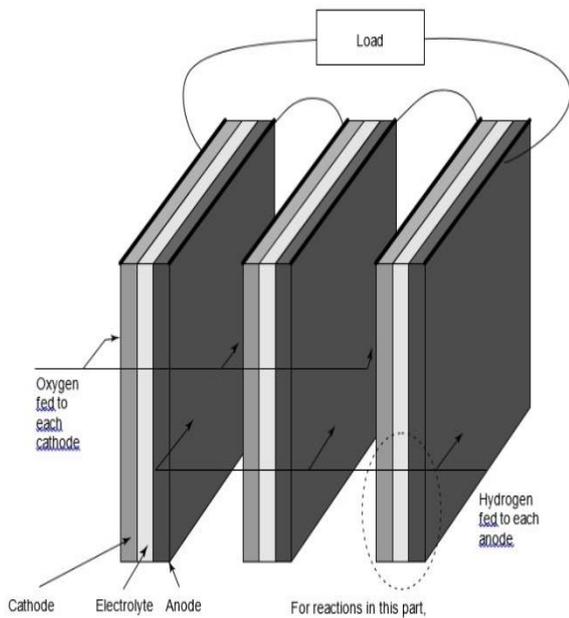


Figure 1.3 Simple edge connection of three cells in series.

The method of connecting to a single cell, all over the electrode surfaces, while at the same time feeding hydrogen to the anode and oxygen to the cathode. The grooved plates are made of a good conductor such as graphite, or stainless steel. To connect several cells in series, 'bipolar plates' are made. These plates – or cell interconnects – have channels cut in them so that the gases can flow over the face of the electrodes. At the same time, they are made in such a way that they make a good electrical contact with the surface of each alternate electrode. However, the design of the bipolar plate is not simple. If the electrical contact is to be optimised, the contact points should be as large as possible, but this would mitigate the good gas flow over the electrodes. If the contact points have to be small, at least they should be frequent. However, this makes the plate more complex, difficult, and expensive to manufacture, as well as fragile.

Ideally the bipolar plate should be as thin as possible, to minimise electrical resistance and to make the fuel cells stack small. However, this makes the channels for the gas flow narrow, which means it is more difficult to pump the gas round the cell. This sometimes has to be done at a high rate, especially when using air instead of pure oxygen on the cathode. In the case of low-temperature fuel cells, the circulating air has to evaporate and carry away the product water. In addition, there usually have to be further channels through the bipolar plate to carry a cooling fluid. Some of the further complications for the bipolar plate are considered in the next section.

**D. Gas Supply and Cooling**

The arrangement shown has been simplified to show the basic principle of the bipolar plate. However, the problem of gas supply and of preventing leaks means that in reality the design is somewhat more complex.

Because the electrodes must be porous (to allow the gas in), they would allow the gas to leak out of their edges. The result is that the edges of the electrodes must be sealed. Sometimes this is done by making the electrolyte somewhat larger than one or both of the electrodes and fitting a sealing gasket around each electrode. Such assemblies can then be made into a stack,

The fuel and oxygen can then be supplied to the electrodes using the manifolds, Because of the seals around the edge of the electrodes, the hydrogen should only come into contact with the anodes as it is fed vertically through the fuel cell stack.

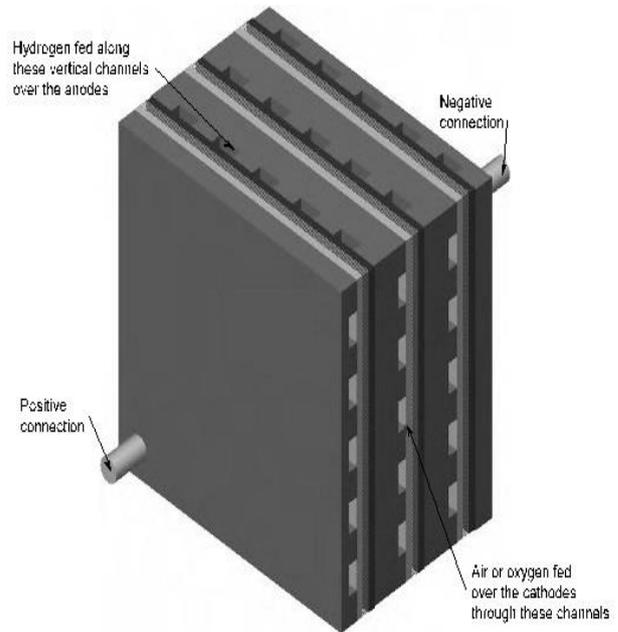
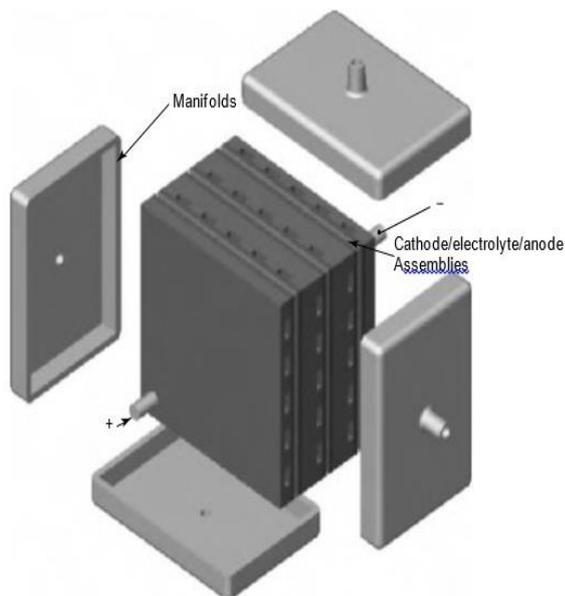


Figure 1.4 A three-cell stack showing how bipolar plates connect the anode of one cell to the cathode of its neighbour.

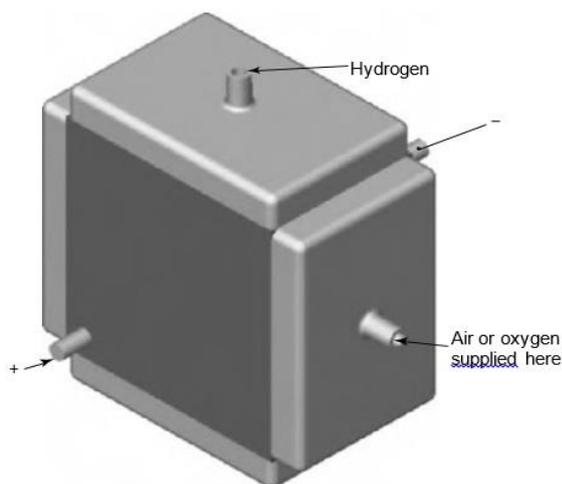
Similarly, the oxygen (or air) fed horizontally through the stack should only contact the cathodes, and not even the edges of the anodes. It is clear that it would be hard to supply a cooling fluid running through the cells. In practice, this type of cell has to be cooled by the reactant air passing over the cathodes. This means air has to be supplied at a higher rate than demanded by the cell chemistry; sometimes this is sufficient to cool the cell, but it is a waste of energy. The second disadvantage is that the gasket round the edge of the electrodes is not evenly pressed down – at the point where there is a channel, the gasket is not pressed firmly onto the electrode. This results in an increased probability of leakage of the reactant gases.

A more common arrangement requires a more complex bipolar plate and The plates are made larger relative to the electrodes and have extra channels running through the stack that feed the fuel and oxygen to the electrodes. Carefully placed holes feed the reactants into the channels that run over the surface of the electrodes. This type of arrangement is called *internal manifolding*. It results in a fuel cell stack that has the appearance of the solid block with the reactant gases fed in at the ends where the positive and negative connections are also made. Such a fuel cell stack is shown, The end plate is quite complex, with several connections. The stack is a solid block. Electrical connections have been made to each of the approximately 60 cells in the stack for testing purposes. The typical form of a fuel cell as a solid block with connections at each end ,The bipolar plate with internal manifolding can be cooled in various ways. The simplest way is to make narrow channels up through the plates and to drive cooling air or water through them. Such an approach is used in several systems. Alternatively, channels can be provided along the length of the cell, and there is provision for this in the system. The preferred cooling method varies greatly with the different fuel cell types

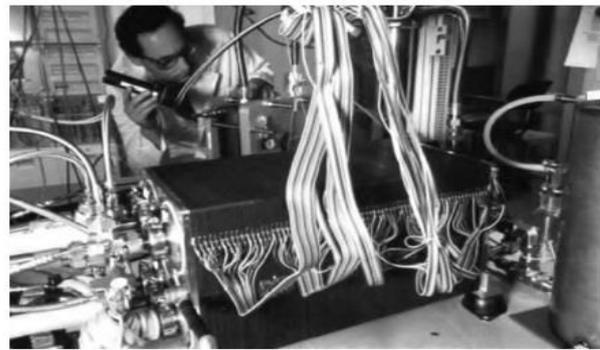


**Figure 1.5 Three-cell stack, with external manifolds.**

It should now be clear that the bipolar plate is usually quite a complex item in a fuel cell stack. In addition to being a fairly complex item to make, the question of its material is often difficult. Graphite, for example, is often used, but this is difficult to work with and is brittle. Stainless steel can also be used, but this will corrode in some types of fuel cells. Ceramic materials have been used in the very high temperature fuel cells. The bipolar plate nearly always makes a major contribution to the cost of a fuel cell. Anyone who has made fuel cells knows that leaks are a major problem. If the path of hydrogen through a stack using internal manifolding is imagined, the possibilities for the gas to escape are many. The gas must reach the edge of every porous electrode – so the entire edge of every electrode is a possible escape route, both under and over the edge gasket. Other likely trouble spots are the joints between each and every bipolar plate. In addition, if there is the smallest hole in any of the electrolytes, a serious leak is certain, when the different fuel cell types are described in more detail, attention is given to the different ways in which this problem is solved.



**Figure 1.6 The external manifolds are fitted to the fuel cell stack. Note that no provision has been made for cooling**



**Figure 1.7 Photograph of a fuel cell stack under test. The voltage of each of the approximately 60 cells in the stack is being measured. Note the carefully engineered end plates. (Photograph reproduced by kind permission of Ballard Power Systems.)**

## E. FUEL CELL TYPES

Leaving aside practical issues such as manufacturing and materials costs, the two fundamental technical problems with fuel cells are

- The slow reaction rate, leading to low currents and power, and
- That hydrogen is not a readily available fuel.

To solve these problems, many different fuel cell types have been tried. The different fuel cell types are usually distinguished by the electrolyte that is used, though there are always other important differences as well. The situation now is that six classes of fuel cell have emerged as viable systems for the present and near future.

In addition to facing different problems, the various fuel types also try to play to the strengths of fuel cells in different ways.

The **proton exchange membrane (PEM) fuel cell** capitalises 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. With a solid and immobile electrolyte, this type of cell is inherently very simple. These cells run at quite low temperatures, so the problem of slow reaction rates is 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.

The problem of hydrogen supply is not really addressed – quite pure hydrogen must be used, though various ways of supplying this are possible. 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 powers, but nevertheless, even at low power, there are many potential applications in the rapidly growing area of portable electronics equipment. Such cells, in the foreseeable future at least, are going to be of very low power, and used in applications requiring slow and steady consumption of electricity over long periods.

Although PEM fuel cells were used on the first manned spacecraft, the **alkaline fuel cell** was used on the Apollo and Shuttle Orbiter craft. 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.

where their main problem is described – that the air and fuel supplies must be free from CO<sub>2</sub>, or else pure oxygen and hydrogen must be used.

The **phosphoric acid fuel cell (PAFC)** was the first to be produced in commercial quantities and enjoys widespread terrestrial use. Many 200-kW systems, manufactured by the International Fuel Cells Corporation (now trading as UTC Fuel Cells Inc.), are installed in the USA and Europe, as well as systems produced by Japanese companies. Porous electrodes, platinum catalysts, and a fairly high temperature (~220°C) are used to boost the reaction rate to a reasonable level. The problem of fuelling with hydrogen is solved by ‘reforming’ natural gas (predominantly methane) to hydrogen and carbon dioxide, but the equipment needed to do this adds considerably to the cost, complexity, and size of the fuel cell system. Nevertheless, PAFC systems use the inherent simplicity of a fuel cell to provide an extraordinarily reliable and maintenance-free power system.

Several PAFC systems have run continuously for periods of one year or more with little maintenance requiring shutdown or human intervention.

As is the way of things, each fuel cell type solves some problems, but brings new difficulties of its own. The **solid oxide fuel cell (SOFC)** operates in the region of 600 to 1000°C. This means that high reaction rates can be achieved without expensive catalysts, and that gases such as natural gas can be used directly, or ‘internally reformed’ within the fuel cell, without the need for a separate unit. This fuel cell type thus addresses all the problems and takes full advantage of the inherent simplicity of the fuel cell concept. Nevertheless, the ceramic materials that these cells are made from are difficult to handle, so they are expensive to manufacture, and there is still quite a large amount of extra equipment needed to make a full fuel cell system. This extra plant includes air and fuel pre-heaters; also, the cooling system is more complex, and they are not easy to start up.

Despite operating at temperatures of up to 1000°C, the SOFC always stays in the solid state. This is not true for the **molten carbonate fuel cell (MCFC)**, which has the interesting feature that it needs the carbon dioxide in the air to work. The high temperature means that a good reaction rate is achieved by using a comparatively inexpensive catalyst – nickel. The nickel also forms the electrical basis of the electrode. Like the SOFC it can use gases such as methane and coal gas (H<sub>2</sub> and CO) directly, without an external reformer. However, this simplicity is somewhat offset by the nature of the electrolyte, a hot and corrosive mixture of lithium, potassium, and sodium carbonates.

## HYDROGEN STORAGE

### A. *The major technological barrier to the development of hydrogen fuel cell cars*

Both from the point of view of global warming and from that of the inevitable exhaustion of the Earth’s oil reserves, it has become highly desirable to develop an alternative energy source for automobiles. Since the development of the PEM (Proton Exchanged Membrane) fuel cell, which is fuelled by hydrogen and oxygen (air) and produces only water, hydrogen has generally been seen to be the most promising approach. However, although the development of fuel cell technology appears to be progressing smoothly towards eventual commercial exploitation, a viable method for storing hydrogen onboard a vehicle is still to be established. The US DoE has taken what is perhaps an extreme view of what the technology needs to deliver. By rejecting taxation as a means of persuading the public to change their fuel, the DoE starts from the position that the hydrogen fuelled vehicle must be able to match the performance of a hydrocarbon fuelled car and must do so at a comparable cost (based on the costs of oil in the recent past). This has led them to establish a series of targets

which, given the remarkable advantages of petrol and diesel for this purpose, will be very tough to meet

Gravimetric energy density: 2 KWh/kg

Volumetric energy density: 1.5 KWh/l

H<sub>2</sub> storage capacity (mass fraction) of 6 wt% (on a system basis)

Operating temperature: -30 to +50 °C

Re-fuelling time <5 min

Refuelling Rate: 1.5 kgH<sub>2</sub>/min

Recoverable amount of hydrogen: 90%

Cycle life: 500 times (requirements for the physical properties of storage material)

From our present point of view, the most significant of these targets are that

1. The fuel tank system when charged should contain 6% gravimetric hydrogen density; and

2. The system should be capable of being recharged at the filling station in less than 5 minutes. In addition,

3. The hydrogen should be available at the inlet of the fuel cell at a pressure of a few bar without it being necessary to heat the store to a temperature of more than 50°C. If (2) cannot be met, we could consider using replaceable fuel tanks that can be recharged off-line at the fuel station. If one goes this way, one should also consider the use of chemical hydrides that will liberate hydrogen on the addition of water [1,2] but here the product would have to be sent back to a factory to be recycled.

Four different methods of hydrogen storage are currently being considered, namely liquid hydrogen, high pressure hydrogen, solid state hydride storage (including chemical hydrides) and porous solid adsorption of molecular hydrogen. The first two methods have reached the engineering prototype stage while for the last two methods, there is still much to be done in selecting the optimum system for further development. This paper will concentrate on the present status of these last two approaches. Before doing that, however, we should discuss the disadvantages of the first two methods, given that they have actually been demonstrated to work.

### B. *LIQUID AND HIGH PRESSURE HYDROGEN STORAGE*

Firstly, liquid hydrogen can be stored on board the vehicle, as has been demonstrated by BMW who have produced a limited series of cars fuelled in this way. In this case, most of the hydrogen is supplied to a conventional Internal Combustion Engine (ICE) with some going to a fuel cell which provides the electrical power for air conditioning etc. This approach yields a gravimetric storage density of 100% H<sub>2</sub>. However, if you include the mass of the tank, this is reduced to about 10% gravimetric H<sub>2</sub>. Moreover, it has two major disadvantages:

1. There is inevitably a boil-off rate which is currently ~ 1%/day;

2. There is an inevitable energy loss due to the refrigeration process which amounts to 30% of the energy available from burning the hydrogen, even in the largest plant size.

The second approach is to store the hydrogen at high pressures. A conventional steel hydrogen cylinder achieves about 1% gravimetric hydrogen. Recent developments of fibre reinforced resin have reached pressures of 700 bar, corresponding to about half the density of liquid hydrogen. The CUTE hydrogen fuelled buses, as have been operating recently in London, actually use conventional steel hydrogen cylinders (150 bars). However, while we are all happy to have buses driving round with high pressure hydrogen cylinders on board – after all, gas suppliers are doing this all the time using properly designed lorries - there are some anxieties about letting the general public loose with the really high pressure cylinders that are now being developed.

## C. METAL HYDRIDE STORE

Turning to metal hydride stores, here the hydrogen split into atoms at the surface of the metal and then enters the metallic lattice in the atomic form, diffuses through the metal, jumping between interstitial sites; and finally forms a hydride phase with a more or less ordered hydrogen sub-lattice. If the (inter) metallic lattice contains *d* or *f* electron states at the Fermi surface, the hydrogen *s* electron can be partly donated to the conduction band and the bare proton, screened electrostatically by electrons at the Fermi Surface, can move relatively freely through the lattice. Most binary or intermetallic hydrides are either very stable or very unstable but a number do show an equilibrium hydrogen pressure at room temperature of about 1 bar.

The prime example of such a system (apart from palladium, which is rather too expensive!) is lanthanum nickel hydride (LaNi<sub>5</sub>H<sub>6</sub>) and subsequently, its use in rechargeable metal hydride batteries operated in KOH was demonstrated. LaNi<sub>5</sub>/H is not itself a practical system for a battery as the lattice tends to fragment after a few hydrogenation cycles but, in the following years, a series of AB<sub>5</sub> compounds based on this system were developed, mainly in Japan. Batteries made from these compounds (called Nickel - Metal-hydride (NiMH) batteries), have largely replaced Ni-Cd rechargeable batteries. Indeed, in China, which has large deposits of rare earths, bicycles with electric motors powered by metal hydride batteries are in mass production. However, batteries on their own have to be recharged by plugging into the mains electricity over night and AB<sub>5</sub> compounds can only provide about 1% hydrogen by mass – so, while they have a role for powering bicycles, they do not seem capable of providing a long term substitute for petrol or diesel fuel.

The hunt is therefore on to find lighter metal lattices that will work as well as these AB<sub>5</sub> materials while satisfying the gravimetric storage requirement. However, there are a number of major problems that will have to be dealt with. Firstly, the protonic transport system that works for the transition metal hydrides (where the metal atom effectively changes valency as the hydrogen is added) is not available where the bonding is either ionic (H<sup>-</sup>) or covalent - because here the chemical reaction involves the transfer of integral numbers of electrons. Hence the addition of hydrogen must involve the complete geometric rearrangement of the lattice. This inevitably results in a much smaller diffusion coefficients for hydrogen in the solid phases and hence a practical system has to involve nanoscale materials with large surface areas. Secondly, most potential systems are rather too thermodynamically stable. This fact has two consequences; firstly the hydrides have to be heated up to an inconveniently high temperature to provide hydrogen at an appropriate pressure and, secondly, the heat of absorption (while recharging with hydrogen) is rather high and this means that a large amount of heat has to be removed during the refuelling process, making it difficult to meet the fuelling time specified by the DoE (5 minutes). Simple calculations show that if the refuelling is to take place in this time, a typical American car would require several megawatts of cooling during the refuelling process. A third difficulty is that the light hydride systems considered so far are all rather strong reducing agents and hence react vigorously with air. Apart from the possibility of dust explosions, this means that the fuel will lose its activity if there is any inward leakage of air. Vacuum-tight engineering will therefore be essential. Here again, the possibility of a system that involves changing tanks at the filling station, as, for example, with Calor Gas, may have to be considered.

## D. SODIUM ALANATE SYSTEM

The first light hydride system to show promise was sodium alanate (NaAlH<sub>4</sub> and Na<sub>3</sub>AlH<sub>6</sub>). Bogdanovich and Schwickardi showed that when these systems are activated using TiCl<sub>3</sub>, the rate of absorption/desorption of hydrogen is much enhanced. The full reaction can be written:



The hydrogen is evolved over two plateaus. The readsorption process also shows two plateaus (3.7% in the first plateau and 3% in the second) but there is considerable hysteresis in this process. The performance can be improved in a variety of ways, for instance by mechanically alloying the material.

This system illustrates nicely the difference between the light hydrides and the traditional transition metal systems in that the hydrogen is evolved as a result of a complete change in the structure in which a single phase (NaAlH<sub>4</sub>) decomposes into the hexahydride and aluminium metal where the two alanate phases have quite different crystal structures. It is quite remarkable that in this process, the Al released collects in precipitates but it is even more remarkable that in the reverse reaction, when hydrogen pressure is applied, the Al precipitates decompose to reform the NaAlH<sub>4</sub> phase. It seems likely that some volatile species is formed by direct reaction of hydrogen with the small Al precipitates and that this allows the reaction to proceed at a reasonable rate. It is also quite difficult to understand the precise role of the Ti – whether it is a surface catalyst or whether it is incorporated in the crystal structure.

## E. LITHIUM IMIDE SYSTEM

A very similar process has been demonstrated in the Lithium imide system, starting from a mixture of lithium amide and lithium hydride [13].

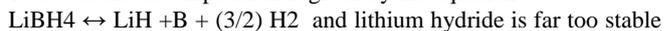


The lithium amide and the lithium hydride can be ball-milled together to ensure that the lithium hydride is close enough to react rapidly with the amide. Alternatively, we can start with lithium nitride and hydrogenate it. Doing it this way automatically produces an intimate mixture of amide and hydride. Here again, there is a volatile molecule that facilitates the reaction. In this case, it is NH<sub>3</sub>.

The disadvantage of the LiN system is that the amide and imide are rather too stable. For instance, the thermal desorption profiles under argon show a first peak at 700K. It is therefore necessary to find ways of destabilising this structure, for instance by adding Mg, which reduces the temperature range for thermal desorption in proportion to the amount of Mg added up to the point where 30% of the lithium has been replaced by magnesium. Here the desorption temperature has been reduced to 350K.

## F. BOROHYDRIDE

A similar system with some potential for development is the borohydride system which shows the highest known hydrogen contents. In the case of lithium borohydride, the hydrogen content is 18.5% by mass but the reversible hydrogen content is actually 13.8% as the decomposition is given by the equation



and lithium hydride is far too stable relative to Li metal to decompose at accessible temperatures. The decomposition above takes place around 573K, which is actually above the melting point of LiBH<sub>4</sub> which is 550K. However, the decomposition process is enhanced by use of a catalyst. For instance, SiO<sub>2</sub> has been reported to reduce the decomposition temperature to 473K. It has also been shown that the rehydriding process will proceed to completion under 35 MPa at 873 K. It is interesting to note that XRD measurements after the decomposition only show small peaks due to LiH. Presumably the boron remains in an amorphous form. Equally, after rehydriding, the peaks corresponding to LiBH<sub>4</sub> are small and rather broad. However, the authors demonstrated that the BrH<sub>4</sub><sup>-</sup> anions are in fact being formed because the characteristic vibrational modes of BH<sub>4</sub><sup>-</sup> are seen in the.



Raman spectra both before dehydriding and after rehydriding. Here again, current efforts are being devoted to surveying different mixtures of alkali cations to see if the compound can be sufficiently destabilised to release and reabsorb hydrogen at lower temperatures and useable pressures. However, given that the hydrogen is part of a covalently-bonded anion, it is not obvious that changing the cation will have a very significant effect on the stability.

An alternative way of using sodium borohydride is to make use of its reaction with water in an alkaline solution in the presence of a catalyst, for instance ruthenium. This process has been developed, for instance, by Millenium Cell Inc.

Here the reaction is



If the solution starts at the maximum concentration, the gravimetric yield of hydrogen is about 7.5%. Because the catalyst is heterogeneous, the solution can be added to start the reaction and then, if necessary removed to stop it. In practice, the product, sodium metaborate solution, would be drained away from the catalyst at the filling station and would be replaced by fresh sodium borohydride solution. The hydrogen produced by this route is ideal for use with a PEM fuel cell being very pure, except for water vapour which is actually necessary to humidify the PEM membrane.

This is a very attractive route for storing hydrogen on board a vehicle. The solution of sodium borohydride is quite inert – clearly safer than gasoline. The main problem is the cost of the borohydride which is quoted to be \$80/kg. Thus the main research activity in this area is in the development of alternative processes for regenerating NaBH<sub>4</sub> from the NaBO<sub>2</sub>, presumably at some central plant. However, it must be realized that the heat released, 75kJ/mole H<sub>2</sub> is not used directly for propulsion so that the efficiency of the process is inevitably somewhat limited in energy terms. Thus, while being very attractive for small portable devices, this process still seems somewhat impractical for vehicle propulsion systems.

### G. MAGNESIUM HYDRIDES

Magnesium hydride is the most studied of the light hydrides as it is potentially cheap. The stoichiometric material suffers from both rather high stability and very slow hydrogen absorption/evolution due to low hydrogen diffusion constants in the bulk. The obvious remedy to low diffusion rates is to reduce the particle size by ball-milling (the evolution time being approximately  $l^2/D$ , where  $l$  is the particle dimension and  $D$  is the chemical diffusion coefficient). Indeed, 15 minutes of ball milling of the as-received material reduces the evolution time to about 2000 sec at 575 K and 0.1 kPa. However, a very much more dramatic reduction in the evolution time can be achieved by adding about 10% by weight of nanoscale Nb<sub>2</sub>O<sub>5</sub>. Here, after 15 minutes of ball milling, the evolution time is reduced to about 100 sec, a practical value. Re-absorption took place at 1 MPa at 300°C. This suggests that MgH<sub>2</sub> is rather too stable and that this is not significantly affected by the addition of the Nb<sub>2</sub>O<sub>5</sub>. However, it is possible that a lower stability compound can be produced by starting from a magnesium alloy or intermetallic compound.

### H. PYSORBED HYDROGEN ON HIGH SURFACE AREA MATERIALS

The other possible method of storage is to physisorb molecular hydrogen on a solid with a high surface area – as in a typical molecular sieve. This approach works well with methane which can be efficiently stored on activated carbons. However, for hydrogen and for heats of adsorption that are typical of Van der Waals interactions, useful storage at ambient temperatures looks

unlikely. In fact, simple calculations show that, at ambient temperatures, the amount stored in a unit volume increases with hydrogen pressure but, at practical pressures, rather less would be stored than would be stored in the same volume of gas at the same gas pressure. On the other hand, if the hydrogen molecule splits into two and each resulting hydrogen atom is chemisorbed, the strength of the chemical bond is normally such that it is impossible to get the hydrogen to desorb at reasonable temperatures and pressures.

There are two possible ways round this difficulty. The first would be to store the hydrogen in an adsorber at 80K. The second is to find a surface where the isosteric heat of adsorption is significantly greater than for the normal physisorption case (about 4 kcal/mole in chemist's units or 40 meV/atom for physicists). Some years ago, a great deal of excitement was generated by reports that very large amounts of hydrogen could be stored on carbon nanotubes and carbon nanofibres at room temperature, suggesting a dramatic increase in the heat of adsorption but these results have not proved to be reproducible.

Consider first the use of a store kept at nitrogen temperatures. The amount of hydrogen stored on a surface can be measured using either a gravimetric or volumetric technique. Comparative gravimetric and volumetric data show comparable isotherms. These have a typical Langmuir shape, suggesting that the asymptotic mass adsorbed corresponds to a monolayer coverage. It is not surprising that multi-layer coverage is not clearly seen so far above the boiling point of liquid hydrogen. Obviously, in measuring the uptake of hydrogen at 80K, one has to be careful that no other gas is present. Some of the early spurious results were probably due to irreversibly trapping water vapour. It is clearly essential to first bake out the sample at high temperature and then to confirm that the measured isotherm is reversible. An interesting point to note about the gravimetric technique is that, before correction for the buoyancy effect (due to different masses of gas being displaced by the sample and the counter balance), the mass adsorbed first increases along a typical Langmuir-type isotherm but then begins to lose mass linearly due to the uplift of the gas around the sample. If the buoyancy correction is made correctly, the corrected curve will tend asymptotically to a maximum amount of gas adsorbed as expected for a Langmuir isotherm. However, the useful effect of the adsorber (the improvement in storage compared to a pressurised gas in an empty volume) is given by the actual increase in the weight of the sample without buoyancy correction.

As would be expected for a limiting monolayer coverage, the mass of hydrogen adsorbed at 80K turns out to be proportional to the surface area as measured using the BET (Brunauer, Emmet and Teller) method, more or less regardless of the nature of the surface, being about 2.5% per 1000m<sup>2</sup> surface area. However, at ambient temperatures and 20 bars pressure, only about 7% of the 80K mass is adsorbed. While manufacturers would be reluctant to operate a fuel tank at 80K, such a system would have significant advantages over a liquid hydrogen store at 20K in that the refrigeration costs would be about 25% of those at 20K and the boil-off would be slower and could be accommodated by allowing for a slow increase in overall hydrogen pressure. Further, because the heat of adsorption is small, heat release during fuelling is not a problem. Also, in accident conditions, the rate of release from a porous store would be much slower than from a liquid hydrogen or gas pressure storage system. In order to have any serious chance of a viable molecular hydrogen storage system, one would need to develop a surface that has a higher heat of adsorption than a typical carbon surface and hence we need to understand the physics of the surface interaction on a well-defined surface such as carbon nanotubes.

The physics of this process can be investigated in a very direct way using Inelastic Neutron Scattering [24, 25]. The beauty of this method is that the inelastic scattering is dominated by the para-ortho inelastic neutron scattering cross section. If the SWNT (Single-Walled Nano Tube) sample is held at 20K or so, all the hydrogen converts into the para- state with zero angular momentum ( $l=0$ ). Using the high resolution TOSCA spectrometer at ISIS at the Rutherford Appleton Laboratory - which measures neutron energy loss processes down to a final energy of 3.5 meV, we can measure the neutron energy loss cross section associated with exciting para- molecules ( $l=0$ ) to ortho- ( $l=1$ ) states, which for free molecules, would involve a neutron energy loss of 14.7 meV. However, the measurements (Fig 1) show a complex peak shape, suggesting one or more non-spherical potential energy wells at the trapping site. By measuring this spectrum as a function of hydrogen coverage, it was concluded that there were at least two different surfaced sites. The first to be filled, attributed to a groove site where two surface nanotubes touch, corresponds to a split peak (13.5 and 15.1 meV with a 2:1 intensity ratio). The second, at 14.5 meV (unsplit) is attributed to sites on the external convex surface of the nanotubes. As the surface coverage exceeds 100%, a third peak appears at about 14.6meV which is attributed to a second layer of molecules. By comparing the temperature dependence of the relative intensity of the groove site peaks with the other two features as a function of hydrogen coverage, it is concluded that the former have an isosteric heat of H<sub>2</sub> adsorption of 75 meV compared with 35 meV for the external convex surface. This compares with 39 meV on the equivalent site on a graphene surface. It is interesting to note that the reduced energy peaks of the groove site imply a slight increase in the H-H distance and corresponding increase in the moment of inertia. This corresponds to a slight reduction in the zero point energy of the rotational states which presumably contributes to the increased heat of adsorption on these sites. This immediately suggests that surfaces can be produced that increase the strength of the interaction so as to increase the H-H distance by a much greater amount. Such an interaction might also give rise to a reduction in the zero point energy for the H-H vibration frequency which could give rise to a significant increase in the trapping energy.

The search for a viable high surface area storage material has of course extended from carbon systems to, for instance, zeolites, Metal Oxide Frameworks (MOFs) and other materials developed for use as catalyst supports,

*A. An overview to the hydrogen fuel cell vehicle as shown in figure below:*

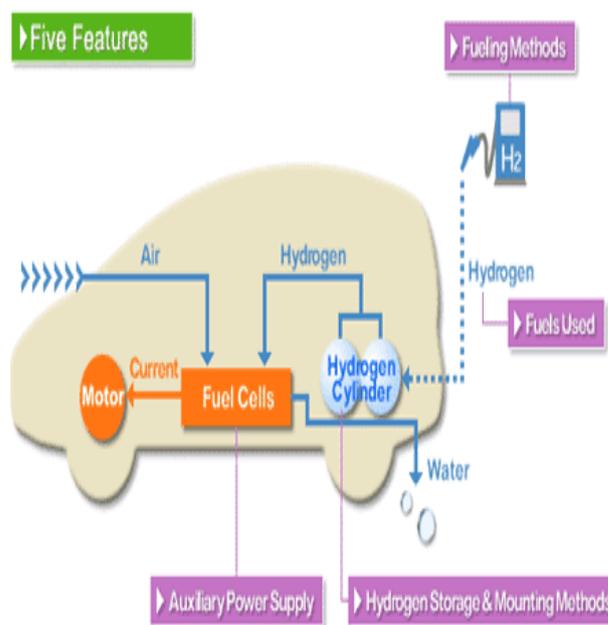


Fig 2.1 shows hydrogen fuel cell vehicle.

Differences In Energy Efficiency Among Automobile Types

Type	Energy source	Overall energy efficiency
Fuel-cell vehicle	Hydrogen produced from natural gas	40%
Hybrid vehicle	Gasoline refined from crude oil	34%
Electric vehicle	Electricity generated at thermal power station using natural gas	33%
Gasoline vehicle	Gasoline refined from crude oil	19%

Source: Toyota

Fig 2.2 Table showing the difference in energy efficiency among automobile types.

Acceptance of FCEV

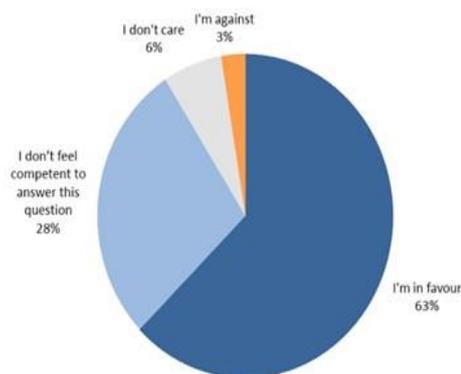


Fig 2.3 Graph showing the acceptance of FCEV.

## CONCLUSION

The search for a material that is capable of storing hydrogen in the amounts necessary to make a hydrogen-fuelled fuel cell vehicle a practical proposition has become a major objective of materials research. The DoE targets of 6% by mass, combined with adequate rates of refuelling the vehicle, will clearly be very tough to meet. Whether the solution is found amongst the light hydrides or through a porous store kept at 80K, the challenges for maintaining the storage material in an active condition will pose a considerable in the engineering of a satisfactorily vacuum-tight containment.

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