CHAPTER 3 - FUEL CELLS WITH HYDROGEN STORAGE TANKS

A *fuel cell* can be regarded as a battery which can be continually fed with fuels from tanks and in which the fuels react to some other product. For submarines we are talking about hydrogen and oxygen as the fuels, and water as being the product. At present both the manufacture and storage of hydrogen cause problems.

Fuel cells need to be distinguished from *redox storage batteries* which also look like batteries fed with fuel from tanks. However in this case valance changes take place in the liquids, releasing energy. The system can be recharged by putting the energy back in at some suitable later stage. There is no irreversible reaction to a product material in this case. Redox storage does not seem suitable for submarines at the moment because the energy density appears to be rather too low. Redox storage, so far as I understand it, is a major invention in electrical practice and it could very well re-appear as a factor in the design of submarines. Ref (6)

Fuel cells, like Stirling engines, have been waiting in the technological wings for many years without ever really being able to find a good market on the back of which their development could be funded. Nevertheless, some slow but steady development has taken place over the last thirty years, helped to some degree by new developments in ion selective membranes which were needed for other purposes in the chemical industry. Fuel cells had some early application in space craft, and are gradually finding niche markets. The major manufacturers hope that tax breaks will be given, either in cities or bigger regions, which will enable them to sell fuel cells to car manufacturers.

Great efforts are being made to promote a sort of transport economy based on hydrogen. It is said that this will be able to take over when oil runs out, that pollution will be less and so on. People talk about hydrogen as though it were a primary energy source. But it isn't. You can't get it out of a hole in the ground. The problem is that at the moment, there is no decent way of making hydrogen other than getting it from some other hydrocarbon, or hydrogen rich carbon compound. Thus you replace universal pollution production (a lot of car engines) with localised pollution in a hydrogen factory on the edge of town. Roughly the same amount of carbon dioxide is made, whether you convert the hydrocarbon to hydrogen and then burn it in a fuel cell, or whether you stick it straight into an internal combustion engine.

In theory, you can make hydrogen from water using light as the energy source and some sort of catalyst to help you over various energy barriers to reaction. In practice no one know how to do this yet, or at least, not in an engineeringly meaningful way. If the problem is solved, then perhaps fuel cells will become important and cheap. Even then, I am not sure why I could not stick the hydrogen straight into a suitably designed heat engine. In the meantime, fuel cells are rare, very expensive and only moderately robust. As far as road transport is concerned we have a classic case of an Emperor With No Clothes.

Fuel cells seem as though they would be an ideal propulsion system for a submerged vehicle. Submarine designers have been mainly concerned in recent times with something called the PEM fuel cell, the acronym standing for "Proton Exchange Membrane". What this means is that a proton, which is a hydrogen ion H^+, can go through the membrane and nothing else can. A device can be made with layers of carbon and membrane which will produce electricity.

In operation you simply feed hydrogen and oxygen into the cell and you get DC electricity out. At low powers the efficiency can be high. The more power you take from the cell the less efficient it becomes. This has led to some lively arguments between fuel cell manufacturers and protagonists of other systems. It is important not to get too hung upon the detail of such figures, since we know that you can make a reasonable submarine drive with a fuel cell.

Although there are some integration problems resulting from the variable voltage of the fuel cell, and matching this up with the motor, you can certainly think to make this the drive system of the submarine. As there is only water as a by product, you have a silently operating drive which is depth independent and which exhausts only fresh water (if indeed you choose to exhaust the water).

The oxygen to fuel one side of the fuel cell can come from a LOX tank just like any other AIP system. All we have to do is to find a way of getting the hydrogen into the boat. Unfortunately, this turns out to be a devilishly tricky matter. Fuel cell driven submarines seem to suffer from reduced range as compared with all other systems.

The PEM fuel cells mentioned above are not the only candidates for a fuel cell. Trials of an alkaline fuel cell were carried out in a German submarine in the 1980's, and there is another type of cell under development called a solid oxide fuel cell which might blossom into a candidate. This latter type has the potential to burn something other than hydrogen as the fuel, say something like methanol, and therefore is pointing at the main weakness of the PEM membrane, that of storing hydrogen. Of course, you don't get something for nothing, and such a fuel cell would have waste products other than water which would have to be disposed of somehow.

Let us just think about an imaginary submarine with a PEM fuel cell and tanks of both liquid oxygen and hydrogen. Consider the basic arithmetic of a 50 % efficient fuel cell. The higher calorific value of hydrogen is 285 kJ/mole so that a 50 % effy fuel cell burning one mole/sec of hydrogen (Molecular weight=2 grams) produces 142.5 kW of electrical DC power. Put another way 1 kWe needs 7.017×10^{-3} moles H2/sec. Decent AIP submarines generate 200 kWe in their AIP plant, so that the submarine would be burning 1.4 moles H2/sec or 5052 moles/hour. This is 10 kg/hr.

The density of liquid hydrogen is extraordinarily low, which you can see in a table in an appendix to this chapter, say 0.07 kg/litre. So every kilogram needs 14.28 litres of liquid before the tank features are added. For a submarine tank you should reckon on something like 17 litres/kg.

The reaction inside the fuel cell is

$$2H_2 + O_2 = 2H_2O$$

4 grams H2 react with 32 grams oxygen

so for every 1 kg of hydrogen burned there are 8 kg of oxygen needed or (remembering that 1 Kg of LOX needs about 1.8 Litres of storage)

17 litres of H2 storage and 14.4 litres of oxygen storage are needed per kg of H2

or for an hour's running we need about 314 litres or 0.314 m3. Now that a bit of experience has been built up we know that we might be able to assign 40 m3 of storage space in an AIP submarine to the fuels. Thus a boat might run for 40 m3/0.314 m3/hr = 127 hours or 5.3 days.

This calculation reveals that although hydrogen has an extremely high energy content per gram (142 kJ/gram) compared with diesel fuel (43 kJ/gram) this is offset by the very low density of liquid hydrogen (0.07 kg/litre) compared with diesel (0.880 kg/litre).

The advantages of running a fuel cell on hydrogen and oxygen are so great however, that the designers were determined not to let a few facts (such as those embodied in the above calculation) deter them.

Two approaches were made to the problem (1) Do better at storing hydrogen (2) Make the hydrogen out of something else inside the boat. Hydrogen is usually made by a process called reforming, which I will discuss in the next chapter.

Methods of storing hydrogen

At the moment there are only a small number of ways of storing hydrogen, and to compare them we can try to work out a number called the storage factor.

(1) Storage in gas cylinders

The K type cylinder mentioned in the chapter on oxygen storage has an external volume, allowing for the packing interstices, of 0.08875 cu m, it has a tare weight of 64 kg and contains 0.6 kg of hydrogen when pressurised to 175 Bara.

To store 1 kg of hydrogen we need 108 kg of cylinder
or 146 litres

(2) Storage as liquid hydrogen in tanks

A small tank for use in a BMW experimental car had length 0.60 m od= 0.566 and held 120 litres LH2 and had a total weight when full of 60 kg so that the storage factors are

To store 1 kg of H2 you need 7.1 kg of tanks
or 17.0 litres

For an industrial sized tank, I think that a reasonable estimate for storing LH2 in tanks is

To store 1 kg of hydrogen we need 6.0 kg of tank
or 14 litres

LH2 tanks need more insulation than LOX tanks because the LH2 is at only about 20 °K as opposed to LOX at about 90 °K. Furthermore the latent heat of evaporation of LH2 is very small perhaps 0.882 kJ/mole at 20 °K as compared with LOX 6.08 kJ/mole at 90 °K. Thus a given heat leak into the tank is going to cause a relatively large boil off.

The ability of a tank to store liquid oxygen can be assisted by putting a re-refrigeration unit on the top, thus re-liquefying some of the evaporating vapour. I have explained this in the chapter on oxygen storage, and it may be that the system could be profitably employed on a submarine LH_2 tank.

(3) Storage in a metal hydride

Hydrogen will go into solution in some metals and metal alloys. Ref (3) The classic cases which have been known for a very long time are platinum and palladium. To absorb one gram of hydrogen, for example, at 1 Bara you could use 160 grams of palladium.

You can't use palladium in bulk jobs, it costs the earth, there isn't a large world total stock and it is very heavy. But, nature having given us a clue, we can look around for other alloys which might absorb hydrogen and in fact several alloys have been found, their selection seemingly owing all to intuition and little to theory. As a matter of fact the status of hydrogen inside the alloy still appears to be unclear, in some cases I, at least, am not sure whether the hydrogen is adsorbed as whole molecules, or atoms, or is present in some electron stripped form.

There are two leading alloys Fe/Ti and Mg+minor components. The weight storage factors are

To store 1 kg of H2 you need 56 kg of tank containing FeTi Ref (2)
or 13.5 litres

Bearing in mind that Mg absorbs much more hydrogen (7 % as opposed to 2 %), we can infer the following storage factors for Mg by putting the appropriate amount of metal in a tank one and a half the size of that quoted in Ref(2)

To store 1 kg of H2 you need 20 kg of tank containing Mg
or 23.2 litres

and these figures take into account all the tankage.

There is always some heat to be controlled. When hydrogen is absorbed by an alloy, heat is given out. Equally desorption requires some heat to be put in. To give you an idea : To desorb one mole of hydrogen from a Ti/Fe some 38 kJ are required. Ref (1) (Compare this with the 248 kJ of thermal energy in the hydrogen)

These hydrogen absorbing alloys behave rather differently. Ti/Fe is much heavier than its magnesium competitor, but a lot of the hydrogen can be extracted by pressure reduction alone rather than having to raise the temperature to 250 °C. Ti/Fe breaks up into a very fine power the first time it is charged with hydrogen, and the design of the system has to reflect this.

In the example of a submarine above running for 5.3 days we had 1.272 tes of hydrogen and if this were dissolved in a magnesium alloy, we should need about 43 tes of magnesium. The problem is that to get the hydrogen out we would have to heat the Mg alloy to 250 °C. The specific heat of magnesium is about 1.0 kJ/kg or 1 MJ/te and so we should have to find $1.09.10^{+10}$ J of energy just to recover the hydrogen from its store. We also have to add the desorption energy which would be about $2.28.10^{+10}$ J a total of 3.37.10+10 J. It is worth doing this because the hydrogen contains about $1.81.10^{+11}$ Joules Remembering that diesel fuel holds about 43 kJ/gram, then you would need to burn about 530 kg of diesel to recover the hydrogen.

Although the arithmetic looks sensible, it is quite difficult to think how you would raise the metal to temperature in a submarine. On one side the magnesium tanks would be cooled by the sea, and on the other they would have to be heavily insulated to stop the crew of the submarine getting cooked.

For these reasons an alloy like Ti/Fe is preferred for use in submarines. Here the hydrogen can be recovered more or less by manipulating the pressure, and the only heat that has to be supplied is the heat of desorption.

At the moment, the weight of the Ti/Fe hydride storage seems to make it difficult to design a plug in section that would be neutrally buoyant. They are always heavy, and this means that retrofitting is difficult. It seems that the submarine had better be designed from scratch.

So if you want a plug you probably can’t have a hydride powered fuel cell.

(4) Other technology

The hydride technology described above can be regarded from a functional point of view as a sort of scientific trick to get liquid hydrogen at room temperature. The strange thing is that the densities of these artificial liquid hydrogens are very close to real liquid hydrogen.

You would think that a liquid was pretty near as dense a state as you could get. We know that liquids have holes inside themselves, because they get less dense as the temp goes up and are in any case a bit less dense than the solid. Nevertheless they do seem as though they have a density pretty near the maximum.

However there are two things to bear in mind. Firstly the hydrogen molecule is made up of two atoms which being separated are each very small and can fit into the funny shaped little cavities between the relatively gross metal atoms. It does seem as though molecular hydrogen (H_2) often splits into atomic hydrogen (H) when it enters a metal alloy.

Secondly you must remember that a hydrogen atom is strange in that it has only one electron on its nucleus. If you take away its electron, there is only the vanishingly small nucleus left. I certainly tend to think that in some alloys such as the 60:40 Pd/Ag alloy used for diffusing hydrogen, that the molecular hydrogen is both dissociated and then ionised.

At all events, we have some idea from measurements that we can have dense hydrogen at near to room temperature, and this has led researchers to wonder whether a material might be found that stored hydrogen at a density comparable with the liquid, which was much lighter than Fe/Ti and from which the hydrogen could be detached without raising the temperature very much.

A clue to one line of attack came from the fact that it was known that hydrogen could be stored on cooled carbon at –120 °C. Quite a lot of hydrogen could be captured in this way, up to 10 % by weight of the carbon as opposed to the best hydride which when charged only had about 7 % of hydrogen. Although this observation could not be engineered into a proper storage system it led, in due course of time, to something else.

Much to most scientists' astonishment, in the last few years a completely new mass produceable form of carbon has been discovered which is neither graphite or diamond. It appeared first in Kroto and Smalley's work as little balls consisting of sixty carbon atoms joined together to make an entity that looked a bit like a football. Ref(4) This material was called buckmasterfullerene after an architect who designed structures which looked very similar. Later it became clear that you could make other related structures. The Japanese scientist Sumio Iijima found that you could make tiny carbon tubes. Ref (7). These are called Carbon Nanotubes, the nano coming from their characteristic diameter of the order of 10^{-9} metres.

It would be no very great surprise if these new forms of carbon absorbed hydrogen to some degree. Perhaps what was not expected was that the carbon nanotubes could absorb a great amount of hydrogen at room temperature. See for example Ref 5. True, it appears at the moment that you have to heat them up to 300 °C to get the gas out again, but it is step in the right direction. It would appear that might be able to have a tank of these nanotubes which has about half the energy content of a tank the same size holding diesel fuel.

I think many readers may not understand the extent to which chance may play a role in scientific advance. The discovery of these new forms of carbon did not come about because chemists were successful in trying to make some targeted structure. Rather, Professor Kroto was trying to identify some strange fragments of matter, traces of which he could see in the spectrum of light emitted by stars. Following his nose, as he puts it, and collaborating with many colleagues in the UK and USA, eventually led him and his co-workers to this astonishing discovery.

In Britain, during the Thatcherite years, it was decreed that University research had to be "useful" and that scientists following their instincts in basic untargeted work were to be starved of funds. It was a crazy policy. Nearly every piece of technology we use was brought into being by men following their own ideas. It is regrettable that no-one in the University administrative structure has had the guts to try to overturn the system which pretty nearly guarantees technological stagnation.

A submarine with a fuel cell and stored hydrogen

We have a very good idea what a submarine will look like if it is powered by a fuel cell which derives its hydrogen from a hydride, because the Germans are in the process of constructing the first boat in the 212 Class. Quite a lot of information is put out on their web site at naval-technology.com/projects/type212.

The salient features are that that both the LOX and the hydride stores are placed outside the hull. In order to make space for them the pressure hull is made in two different diameters with a cone shaped joining piece, which houses the fuel cell itself. The German designers have not restricted themselves to considering only the AIP propulsion. They have installed a Permanent Magnet DC propulsion motor and they have dispensed with the lead acid batteries that have been used for eighty years and put in high density sodium sulfide batteries. Both of these items are right at the start of their industrial development and represent a substantial improvement on what went before.

Permanent magnet motors represent quite a new development. They are motors in which high strength permanent magnets are attached to the rotor. The rotor assembly then has no currents flowing in copper wire windings and so does not get hot and so, in turn, does not need cooling. No brushes are needed. The motor can be very much smaller for a given power; they can be about a quarter of the weight and volume of wound motors. The efficiency of the motors can be maintained at high values over a wide range of speeds. Some quoted downsides are the high cost and the fact that if the computer control system goes down you can't run the motor. A normal motor with brushes for example can often be got working by handwork after a failure.

You have to admire the design of this submarine; it represents a package of improvements which together have raised the design on to a new higher plateau. It fascinates me, a Briton, to understand how the Germans managed to carry through this project over such a time scale without all or part of it being scrapped by the arrival of successive defense ministers. We find it difficult to carry out long term technical development unless there is a really exceptionally strong industrial constituency.

The Type 212 submarine is not without its potential problems. It seems from the design, that the engineers are banking on improvements appearing in the hydrogen storage systems. The 212 appears to be restricted in its range which is quoted at 420 nautical miles at 8 kts or something like 2 – 3 days submerged patrol time. This would of course be extended if the boat was tootling around at 2 kts in a restricted patrol area. But, taken by and large, it seems a small range.

Acts of faith in the general area of fuel cells and hydrogen technology have been poorly rewarded in the past. There is certainly no guarantee that a sufficiently weight compact method can be found of storing the hydrogen, and so far as one can see at the moment, there is no hint that hydrogen can be packed into a volume of less than would be occupied by a liquid hydrogen tank. This would lead you think that hydride based submarines might always be operating at the restricted ranges. You have to remember that the whole idea of having AIP submarines was to *increase* the submerged range as much as possible.

Even this might not turn out to be as serious a matter as it might appear. Even if the hydride idea did turn out to be seriously limiting, the German designers would still have accumulated experience in running the fuel cell in a submarine environment. They might then elect to produce the hydrogen from a reformer which we shall shortly go on to discuss.

I doubt also whether such a submarine is *up down capable*. A fuel cell that is designed to run on pure oxygen, will probably function badly if presented with air. Therefore I think it is unlikely that you could use the fuel cell as an emergency power supply on the surface.

In summary, it seems to me that hydride fuel cell systems are heavy, you can't retrospectively fit a plug, and the range might be on the low side. Having said this, if I were buying a submarine, this would be at the top of my list.

APPENDIX – A PROPERTIES OF SATURATED HYDROGEN

By saturated I mean both liquid and gaseous hydrogen being present together

Molecular weight = 2.0159 grams
Triple temperature 13.95 °K   Solid liquid and gaseous phases all simultaneously present
Critical temperature = 33.18 °K No liquid phase above this temperature
Critcal pressure = 13.1 Bara
Critical volume = 63.6 ccs/mole

T °K	P Bara	Liquid density kg/L or gms/cc	Heat of vapourisation kJ/mole
13.95	0.072	0.077	0.890
14	0.074	0.0768	0.899
15	0.127	0.0759	0.904
16	0.204	0.0751	0.905
17	0.314	0.0742	0.906
18	0.461	0.0732	0.9044
19	0.654	0.0721	0.900
20	0.901	0.0711	0.893
21	1.208	0.0699	0.884
22	1.585	0.0687	0.870
23	2.039	0.0674	0.854
24	2.579	0.066	0.833
25	3.213	0.0647	0.808
26	3.95	0.0628	0.778
27	4.8	0.0610	0.742
28	5.77	0.0589	0.698
29	6.872	0.0566	0.646
30	8.116	0.0534	0.581
31	9.51	0.0506	0.497
32	11.07	0.0459	0.377
33.8	13.13	0.0314	0
Compare with waterstuff		about 1.00	about 40

APPENDIX - ENERGY STORED IN A TANK IN VARIOUS FORMS

I mentioned above that I thought that a submarine powered by a fuel cell and obtaining its fuel from stored hydrogen would be bound to have a short range compared with other candidate propulsion systems. In this appendix I have imagined a 200 kW submarine with a submerged range of 14 days. I have worked out how much diesel fuel would be needed and then seen how much hydrogen energy I can get in the same sized tank. It seems to me that for a given tank size you can only store about 30 pc of the energy that you can obtain from a hydrocarbon fuel.

So, consider a submarine delivering 200 kW at the shaft of a closed cycle diesel, and remember tat similar quantities will apply to both Stirling engines and MESMA systems. The diesel will burn 45 kg diesel fuel/hour and over 14 days this is 14,784 kg which will need a nominal 17 m3 of storage volume. The energy held in the diesel (at 43 kJ/gram) is about $6.36.10^{+8}$ kJ.

Let’s fill the tank instead with liquid hydrogen. Even close to the triple temperature the density of the liquid is only about 77 kg/m3 and so in 17 m3 we can put 1309 kg of hydrogen. The heat of combustion is 142 kJ/gram and so the energy content is $1.85.10^{+8}$ kJ which is only about 30 pc of the hydrocarbon fuel.

We don’t like this perhaps so we can mentally fill the tank with Ti/Fe powder. 13.5 litres of the alloy powder contain 1 kg of hydrogen. Therefore 15.5 m3 contain 1000 kg and 17 m3 contain 1259 kg of useable hydrogen and this contains $1.7.10^{+8}$ kJ, a figure which is similar to the liquid case.

Now fill the tank with the much vaunted carbon nanofibres which I may say, are being touted in every research paper as the hydrogen storage medium of the future and which by implication will let you go water-skiing behind your submarine. The fibres are formed as some kind of mat which appears to be rather un-compact at the moment. The bulk density of recently made materials were quoted at 0.1 kg/litre or 100 kg/m3. Thus in 17 m3 of tank I can put 1700 kg of nanofibres. Researchers seem to agree that a good target figure is to have 5% of this weight as adsorbed hydrogen. So in my 17 m3 tank I have 1700 kg of nanofibres holding 85 kg of hydrogen or $1.2.10^{+4}$ kJ. Maybe I did a mess with the sums, but I seem to have a pitifully small amount of hydrogen in this case.

REFERENCES

Ref(1) O Bernauer and C Halene Journal of the Less-Common Metals 131 (1987) pp 213-224

Ref(2) Udo Wolf, Hans Pommer and Günther Sattler German Maritime Industry Journal No 4 December 1993 pp 34-40 who quote a fully engineered tank containing 75 kg hydrogen in an Fe/Ti alloy, the tank having a total weight of 4.2 tes and a volume of 1 m3.

I processed these figures a bit to get an idea of storage in Mg. In the tank above there must have been about 3750 kg of Fe/Ti alloy powder, so the weight of the tank was 450 kg. If I put in Mg I will only need about 1065 kg, so I think it is reasonable to think of a tank half the length and weight. So I then have 75 kg of H2 in a tank of total weight 1290 kg and 0.5 m3 volume.

Ref(3) Cox "Technology of Hydrogen" Chapter 2 "Metal hydrides as Storage media …" by J J Reilly

***Note :** I need the rest of this reference*

Ref(4) Kroto H W, Heath J R, O'Brien S C and Curl, R F, and R.E. Smalley Nature 318 (1985) p165 et seq

An interesting article can be seen at http://www.chemsoc.org/gateway/chembyte/cib/kroto.htm

Ref(5) Chen P, Wu, X, Lin,J and Tan, K L " High H2 uptake…" Science 285 (1999) pp 91-93 and Liu C, Fan Y.Y., Cong H.T., Cheng H.M. and Dresselhaus M.S. Science v286 5 November 1999 pp1127 - 1129

Ref (6) Ralph Zito USP 5,496,659. Process licensed to National Power Company UK as "Regenesys"

Ref(7) S Iijima "Helical microtubules of graphitic carbon" Nature v354 p56 (1991)

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