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HEALTH & SAFETY
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The Hydrogen Economy - Evaluation of the materials science and engineering issues

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EXECUTIVE SUMMARY

OBJECTIVES

The main objectives were to identify materials issues relating to the widespread use of hydrogen as a fuel.

MAIN FINDINGS

1. Hydrogen is seen by many as the answer to the environmental problems of reliance on fossil fuels for energy needs. A great deal of effort is currently being invested in research into all areas of the hydrogen economy, such as fuel cells, hydrogen generation, transportation and storage.

2. Fuel cells have the potential to provide power for a very wide range of applications, ranging from small portable electronics devices to large stationary electricity production and vehicles covering the whole range of road vehicles and possibly extending to rail, marine and even aviation.

3. The main obstacles to achieving a viable hydrogen economy are costs of producing hydrogen from renewable sources, issues relating to transportation and storage due to the low energy density of hydrogen gas, and the cost and reliability of fuel cells.

4. The main material considerations relating to the use of hydrogen are hydrogen embrittlement, material properties at cryogenic temperatures (due to use of liquid hydrogen) and permeability.

5. A number of new materials are likely to come to prominence in a hydrogen economy; high performance composites are likely to be used extensively for high pressure hydrogen cylinders, new materials, or combinations of materials, may be used for hydrogen pipelines and a range of new materials are currently being considered for hydrogen storage, such as metal hydrides and carbon nanotubes.

6. Due to the effect of hydrogen on materials, it is important to test any materials in the environment in which they would be used. Depending on the type of test, this could require the use of very specialist, expensive equipment.

1 INTRODUCTION

Climate change is currently a great concern of many people. In particular, the effect of carbon dioxide emissions, resulting in global warming, from burning fossil fuels is seen as a major problem. The concern spread from environmental pressure groups to governments when the Kyoto protocol was established in 1997, based on principles set out in a framework agreement signed in 1992. Recently, the concern has spread to major business; in May 2005, 13 business leaders from major UK and international companies wrote to the Prime Minister [1] to ask for long term policies aimed at reducing carbon emissions. Significantly, these companies included some that would appear to have a vested interest in the use of fossil fuels, such as Shell, BP and BAA, the British Airport Authority.

An additional problem with fossil fuels is that they are non-renewable, which means that they will eventually run out. The estimates of the remaining reserves vary for the different types of fuel and between different experts. The Hirsh Report [2], produced for the US government, looks at the issues relating to ‘peak oil’ – the time when oil extraction reaches its highest point before declining – and various solutions for mitigating the effects. Half of the predictions for dates of reaching peak oil quoted in the report were before 2010. Reserves of coal and natural gas are significantly larger. A number of steps are being taken to alleviate this problem, such as improving energy efficiency and looking at developing new fuels.

One of the most significant new fuels under consideration is hydrogen. However, hydrogen is not a fuel in the normal sense, as it does not occur naturally but has to be created. It should, more accurately, be seen as an energy carrier. The recent and ongoing advances in fuel cell technology are bringing the widespread use of hydrogen as a fuel closer. It has many advantages over traditional hydrocarbon fuels:

- It is possible to produce hydrogen from renewable sources. The reserves of fossil fuels such as oil and gas are rapidly dwindling and are likely to become scarce in the coming decades unless alternative fuels are widely adopted.

- At the point of use, pollution is greatly reduced, not releasing carbon dioxide or other pollutants. The only waste product from the use of hydrogen in a fuel cell is water.

- It is flexible, able to be burnt in internal combustion engines or converted directly to electricity using a fuel cell. It is the high efficiency and flexibility of fuel cells that is the major driving force behind the use of hydrogen as a fuel.

General safety issues surrounding the hydrogen economy are dominated by fire and explosion concerns, and these issues are relevant to the whole range of aspects of the hydrogen economy, i.e. the generation, storage, transmission and usage of hydrogen.

This report concentrates on the materials issues arising from the anticipated widespread use of hydrogen. The main areas where materials issues arise are in the storage and distribution of hydrogen, although the generation and use may also throw up issues. One of the main problems with using hydrogen as a gas is the low density as compared to fossil fuels, such as oil; the energy per unit volume of hydrogen is much lower. There are a number of possible solutions to this problem, such as storing the hydrogen at high pressure, as a liquid or as a metal hydride. Each of these solutions presents its own materials issues. Other problems associates with hydrogen include permeability and hydrogen embrittlement.

This literature review first looks at what a hydrogen economy might look like. This is an essential first stage to identifying the types of material issues that might arise. To get a view of a future hydrogen economy the range of applications have to be identified. The other aspects of the hydrogen economy are the production and distribution issues. The possible issues relating to materials use within the hydrogen economy are then discussed.

2 HYDROGEN ECONOMY - APPLICATIONS

2.1 ROAD VEHICLES

This is the application that has the highest profile at the moment with a large number of experimental vehicles under development. Most major car manufacturers have a programme to develop fuel cell cars. An investigation by the Breakthrough Technologies Institute for the US Department of Energy identified nearly 20 companies developing light-duty fuel cell vehicles and components at the end of 2003 [3]. They also identified at least 12 companies or partnerships developing or demonstrating fuel cell buses. Indeed, fuel cell buses are now operating on limited trial routes in a number of major cities around the world.

It is not only large vehicles that are being considered for fuel cell power. A number of companies are developing fuel cell powered bicycles and scooters. Some cities where motorbikes and scooters are important modes of urban transport are aiming to restrict the use of petrol versions.

The Department of Transport and the Department of Trade and Industry commissioned a report looking into the stages necessary to move from carbon fuelled vehicles to hydrogen fuelled vehicles. The report, *"Carbon to Hydrogen" Roadmap for passenger cars*, [4] details a number of steps that would enable the goal of fully fuel cell powered cars to be commonly available by 2030. Two routes are described, the low carbon route, which concentrates on advanced diesel engines with hybridisation, and the hydrogen priority route, which proposes the use of hydrogen internal combustion engines together with fuel cell auxiliary power units as an intermediate step.

2.2 OTHER TRANSPORT/VEHICLE APPLICATIONS

2.2.1 Utility Vehicles

A number of utility vehicles have been developed to run on hydrogen. These include a golf cart that uses compressed hydrogen gas and has a range of 250 miles – enough for three days on the golf course. Another company is currently evaluating fuel cells in off-road utility vehicles. These are more powerful than the golf carts and have a range of approximately four hours.

Fork-lift trucks are also being developed. Two systems being developed by Sustainable Development Technologies Canada and Siemens use metal hydride storage to store sufficient hydrogen for eight hours use.

2.2.2 Marine

Fuel cells are being tested as the main power sources for propulsion of sail boats and small motor boats. They are also being used for auxiliary power units. One particularly interesting application is by a company called HaveBlue. Their system incorporates an onboard electrolysis unit to convert water to hydrogen. They claim that with HaveBlue, a sailboat, depending on use, can be virtually energy independent from shore-power and fuel docks. The system relies on renewable power technologies, such as photovoltaic, wind and hydroelectric electricity generation, to provide the power needed for the electrolysis. The water needed is freely available from around the boat and is purified onboard. The hydrogen is then stored for use by fuel cells or hydrogen fuelled internal combustion engines. Using a fuel cell would be more efficient, firstly because they are more efficient than internal combustion engines, and secondly due to the fact that the electric motor used in conjunction with the fuel cells could be used as a generator while under sail, providing an additional power source.

2.2.3 Rail

A mine locomotive, built by the Colorado based Fuelcell Propulsion Institute, has been working in a mine in Ontario, Canada, since October 2002. This has worked well and has pulled loads of up to 20 tonne. The Fuelcell Propulsion Institute is also developing a 109 tonne, 1 MW fuel cell locomotive.

2.2.4 Aviation

Both NASA and Boeing have been investigating the use of fuel cells for aviation purposes. In a feasibility study, NASA concluded that using current state-of-the-art components it would be possible to produce a fuel cell powered craft that could carry 270 pounds (122 Kg) for a distance of 140 miles.

Boeing is looking into a number of different applications for fuels cells. The first application is a fuel cell as the auxiliary power unit. Airliners’ electrical power needs are typically supplied by generating power from the main engines during flight and an auxiliary power unit turbine located in the tail while standing at the airport. Boeing estimates efficiency of 40-45% for in-flight electricity generation and 15% for the auxiliary unit. Efficiencies of a fuel cell based system are estimated to be approximately 75% in-flight and 60% on the ground. This could mean considerable fuel saving with the additional benefits of less noise and air pollution around airports. The proposed system, which could come into service in 2015, would not rely on stored hydrogen, but would reform aviation fuel onboard. [5]

The second application is a light fuel cell powered aircraft. The plane payload will be restricted to the pilot only, as the passenger space will be taken up by the fuel cell. It will not rely solely on the fuel cell, as it will also have battery power.

Advanced Technology Products, base in Massachusetts, is developing a two-seater light aircraft powered by fuel cells. The first phase of the development, running the plane on batteries, has already been completed. The second phase is to run on a combination of battery power and fuel cell, with the final stage being a fully fuel cell power aircraft capable of a range of more than 500 miles.

2.3 SMALL PORTABLE (MICRO FUEL CELLS)

Fuel cells are being proposed as power units for a wide range of portable electrical devices, such as mobile phones and laptop computers. Sanyo and IBM have developed a fuel cell power supply for laptop computers, which they say will be ready for sale in 2006 or 2007 [6]. The system uses methanol as the fuel which would be sold in canisters, allowing instant recharging. However, the system is significantly larger and more bulky than standard batteries, reducing the portability of the computer. IBM and Sanyo hope the system will be popular in offices where intensive computer operations drain battery life quickly, but in this instance, one would expect that a mains power supply would be available and more suitable.

Other manufacturers are also developing small fuel cells. Toshiba have developed a very small fuel cell for use in MP3 players, shown in Figure 1 [7]. The dimensions are 22 × 46 × 4.5 mm, increasing to 9.1 mm thick with the fuel tank. NEC has developed a fuel cell for laptops that is smaller than the system developed by Sanyo and IBM and which may be commercially available in 2005.

All the fuel cells described above are of the direct methanol fuel cell (DMFC) type. These use a mix of methanol and water as the fuel, together with oxygen obtained from the air. It is claimed that the methanol/water mix is no more flammable than vodka. The concentration of the methanol is important; to achieve optimum efficiency, the concentration of methanol should be between 3 to 6%. However, this would necessitate too large a storage tank for portable applications so a higher concentration is used and it is diluted with waste water from the fuel cell.

Figure 1 Small fuel cell prototype by Toshiba

2.4 STATIC/DOMESTIC

Fuel cell technology is also being considered for a wide range of static applications, where fuel cells are used instead of standard internal combustion engine generators, whether for main power generation, uninterrupted power supplies (UPS), or backup generators. There is particular interest in remote communities where electricity from a national grid is not available or unreliable.

The National Renewable Energy Laboratory (NREL) in Colorado, USA, has produced a handbook for residential fuel cells [8]. The handbook is aimed at rural electric cooperatives to help them set up demonstration fuel cell systems in their areas. The systems described do not run directly from hydrogen, but use feedstocks of either methane (piped natural gas) or propane which are reformed onsite. These systems therefore still produce carbon dioxide but are more efficient than standard internal combustion engine generators.

British Gas has recently joined forces with Ceres Power to develop new gas boilers based on fuel cells for domestic applications. The solid oxide fuel cells would use natural gas just like normal boilers, but would provide electrical power in addition to the heating and hot water normally provided.

There is also the possibility of using fuel cells for larger scale power generation. Woking Borough Council are using a fuel cell to generate electricity from natural gas with the waste heat generated by the fuel cell being used to heat a swimming pool complex [9].

While the above examples use methane and therefore produce carbon dioxide, an example of a project that is carbon neutral is the PURE initiative on the island of Unst in the Shetlands [10]. Under their system, wind power is used to generate electricity that is used for heating and to provide power for an industrial estate. Any surplus electricity is used to generate hydrogen by electrolysis. Figure 2 shows a systematic diagram of the electrical/hydrogen system. The hydrogen is then stored ready to be used in fuel cells to generate electricity when the wind power is not available.

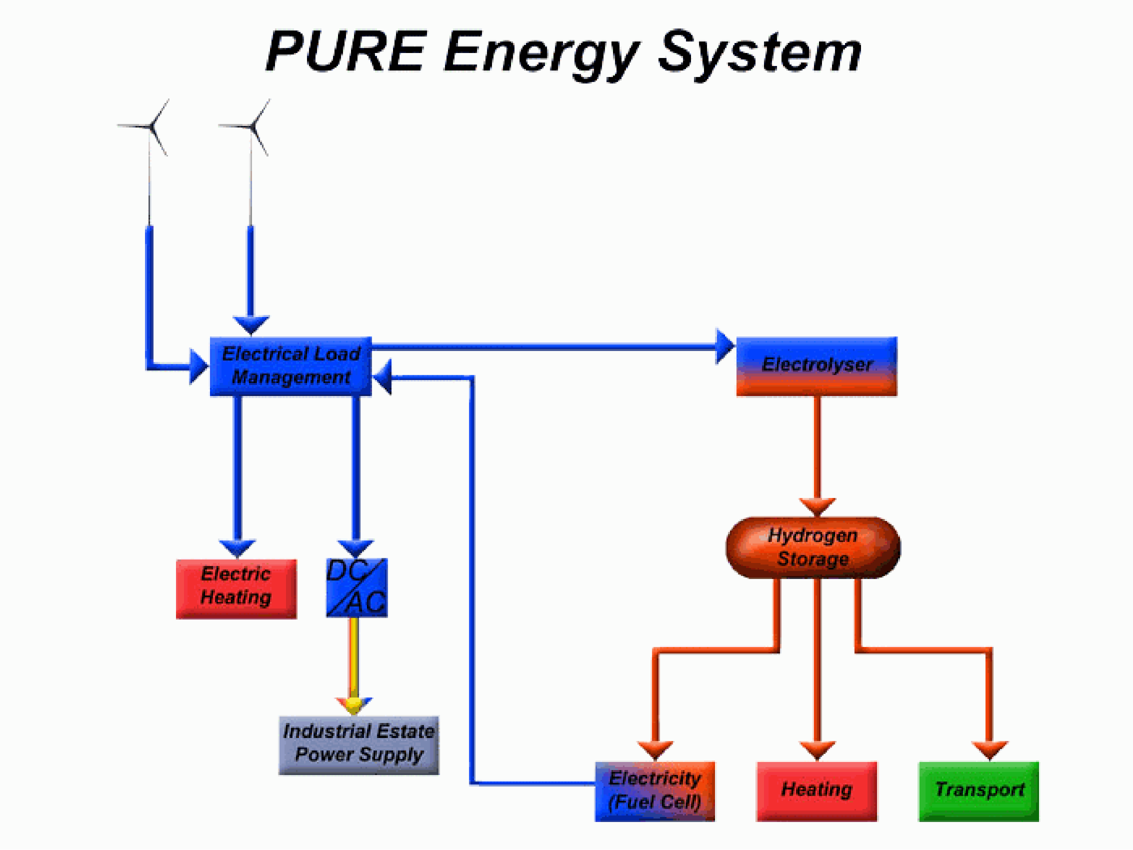


Figure 2 Systematic diagram of the PURE energy system on the island of Unst [10]

3 HYDROGEN ECONOMY - INFRASTRUCTURE

3.1 PRODUCTION LOCATION

Probably the biggest factor affecting what a hydrogen economy would look like in terms of materials issues is the location of hydrogen production. Obviously, there is a need to get hydrogen to where it going to be used; to filling station forecourts, industrial sites, marinas and possibly homes. Unlike petrol, there is the possibility of producing hydrogen at the forecourt from readily available feedstocks (water, natural gas etc.). There are various options for the size and locations of hydrogen production facilities described in the US Department of Energy National Hydrogen Energy Roadmap [11], such as small neighbourhood electrolysis systems, larger reformers in refuelling stations or large nuclear water splitting plants (using high temperature nuclear fission to thermally decompose water).

The advantages of localised production are the avoidance of having to transport the hydrogen to where it is needed, whereas the advantages of large centralised production capabilities are the possible economies of scale available. The National Renewable Energy Laboratory (NREL), a laboratory of the US Department of Energy, looked in detail at the issue of central production versus forecourt production using a range of production processes and distribution methods [12]. For centralised production, their main findings were that:

- The energy intensive liquefaction operation leads to the highest production cost, but the lowest transportation cost
- Pipeline delivery was the most expensive due to the high capital investment needed for pipeline construction, assuming construction of a new dedicated hydrogen pipeline
- Delivery of gas by tube trailer was also expensive due to the low density of hydrogen limiting loads.

These findings broadly agree with an earlier NREL report [13] that looked in detail at distribution and storage costs assuming different distances and production rates. It found that for long distances, liquid transportation was the most cost effective while for short distances gas distribution became more cost effective. Pipeline delivery was only cost effective for very large production rates.

The later report [12] into the economics of central or forecourt production found that the advantages of economy of scale and lower industrial rates for feedstock and power more than compensated for the additional costs of handling and delivery, i.e. central hydrogen production was always more economic than forecourt production. They also found that hydrogen generation based on hydrocarbon feedstocks were more cost effective than generation from renewable feedstocks, such as water or biomass. However, the analysis was performed using current prices for feedstocks and technology. As hydrocarbon feedstock prices rise and technology improves, this situation may reverse.

They suggest that a combination of the three delivery options could be used as the use of hydrogen increases over time. To start with, the small quantities of hydrogen required could be provided by tube trailers. As the demand increases, cryogenic tanker distribution could be used. Once hydrogen has become properly established and volumes needed are higher, pipelines could be used to service regional distribution centres from where tanker or tube trailer distribution could be used.

US based Quantum Technologies are currently developing their HyHauler™ Hydrogen Refuelers. These are mobile units that can be towed to where they are needed. Three versions are under development. The basic system is a store of hydrogen with refuelling capabilities. The HyHauler Plus ™ incorporates an electrolysis system for on-board hydrogen production, which is then compressed and stores the hydrogen. The third variant is a rugged version for military purposes. Air Liquide already has an electrolysis system for on-site hydrogen generation that can produce up to 120 m^3/hour. Each cubic meter of hydrogen requires 3.9 kWh of electricity.

Another alternative is to not use hydrogen as a fuel directly, but a hydrocarbon, such as methanol. This could then be converted to hydrogen using a small on-board reformer before being fed to the fuel cell, or reformed in the fuel cell itself, depending on the type of fuel cell. One type of fuel cell, the direct methanol fuel cell, as its name suggests, uses methanol directly in the fuel cell without any reformation. These fuel cells are likely to be popular for portable electronics devices. Proton exchange membrane (PEM) fuel cells would need a separate reformer to produce hydrogen whereas solid oxide or molten carbonate fuel cells can reform gases such as methane internally, although these high temperature fuel cells are not appropriate for transport applications.

The disadvantage of using hydrocarbons is the fact that carbon dioxide is still produced. The advantages are that the fuel is much easier to transport and store and that the efficiency advantages of fuel cell technology are still there.

3.2 HYDROGEN GENERATION

The methods of producing hydrogen fall into three main categories, thermochemical, electrolytic and photolytic. Within these main categories, there are numerous variations. A lot of research is currently being undertaken with the aim of making these technologies more efficient. There are a number of projects being funded by the Department of Energy [14] in the United States, as well as a number of European projects, funded under the 6th Framework Programme [15].

3.2.1 Thermochemical

This method uses heat and chemical reactions to convert hydrocarbon feedstocks to hydrogen. This is by far the most popular method for producing hydrogen at the current time, but relies on a hydrocarbon source, most commonly natural gas. However, there is the possibility that biomass could be used, and this is being investigated in a European funded project named CHRISGAS. The European Union is also funding a project named HYTHEC that is looking into the feasibility of using thermochemical reactions to convert water to hydrogen.

3.2.2 Electrolysis

By using electrolysis, electricity is used to split water into hydrogen and oxygen, therefore resulting in the useful by-product of oxygen, rather than the unwanted by-production of carbon dioxide as in the thermochemical production methods. The source of the electricity needed could involve CO_2 production, but could also be renewable, such as wind or solar, or nuclear.

There is the possibility that fuel cells could be used in reverse to generate hydrogen, but the optimal conditions for using fuel cells as electricity generators and hydrogen generators are different.

3.2.3 Photolytic

Photolytic hydrogen production technologies use the energy from sunlight to split water into hydrogen and oxygen. Emerging direct water-splitting technologies include photobiological and photoelectrochemical systems.

Photobiological systems take advantage of the fact that some microbes produce hydrogen in their metabolic activities using light energy. By employing catalysts and engineered systems, hydrogen production efficiency could reach 24%. A number of research projects are currently being funded by the US Department of Energy looking at finding the best algae to overcome various problems.

A European project, SOLAR-H, is currently looking at linking molecular genetics and bio-mimetic chemistry to achieve renewable hydrogen production.

Photoelectrolysis uses technology similar to standard photovoltaic (PV) cells to produce a voltage high enough to directly split water into its hydrogen and oxygen components.

3.3 STORAGE

3.3.1 Vehicle Fuel Tanks

One of the main problems when it comes to transporting and storing hydrogen is the very low density of hydrogen. This means that for a given mass of gas a large volume is needed. Nowhere is this problem more apparent than in the area of fuel storage in passenger cars. Drivers are generally reluctant to suffer from having less space, more weight or more cost so designing a system that will give drivers the driving range they want without sacrificing space, weight or significant cost is probably the most demanding of all the storage related problems.

The US Department of Energy has set targets for the performance of storage tanks for road vehicles, to be reached by 2010 and 2015 [16]. The main targets are shown in Table 1. These relate to the volumetric capacity, gravimetric capacity and the cost, all expressed in terms of the energy potential of the hydrogen stored, in kWh.

Table 1 US DoE targets for vehicle hydrogen storage tanks

Target	*2010*	*2015*
Volumetric Capacity (kWh/L)	1.5	1.7
Gravimetric Capacity (kWh/kg)	2	3
System Cost ($/kWh)	4	2

There are other targets, covering aspects such as operating temperature, speed of response, fill time, fuel cost and loss of hydrogen. Current levels of performance for a range of different technologies are shown in Figure 3 and Figure 4. In terms of the three main performance targets, liquid hydrogen appears to be the closest to meeting the targets, but this is let down by the cost of liquefying the hydrogen. Also, the technology for storing liquid hydrogen is relatively mature, so significant improvements in any of the three main areas are unlikely. Significant advances in storing hydrogen as a high pressure gas are also unlikely, as hydrogen does not obey the ideal gas law. Doubling the storage pressure from 70 MPa to 140 MPa would only realise an increase in density of about 50%.

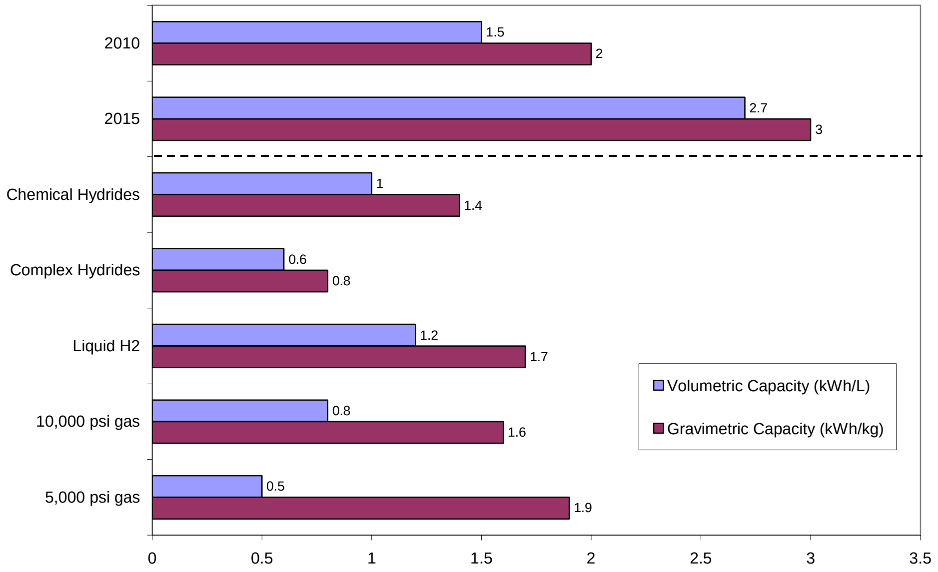


Figure 3 Status of current technologies relative to key performance targets

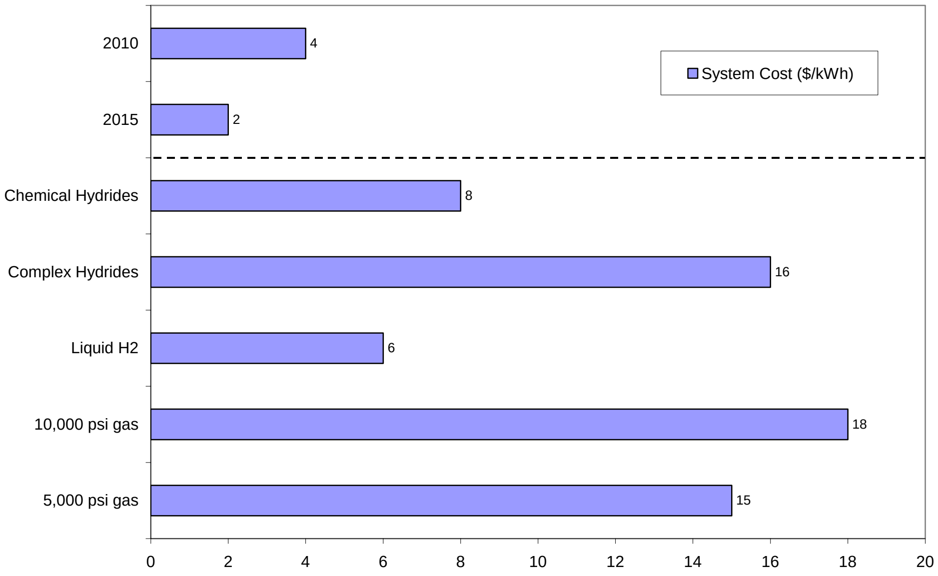


Figure 4 Status of current technologies relative to key cost target

A major problem with storing hydrogen as a liquid on board vehicles is evaporation losses. It is estimated that an entire tank of liquid hydrogen could evaporate in just 3 weeks, leaving a tank of low pressure hydrogen gas that would not be able to propel the car any significant distance. A solution being developed by Lawrence Livermore National Laboratory is to combine high pressure and cryogenic storage in one tank. Their design consists of a conventional aluminium lined, composite high pressure cylinder surrounded by many layers of polyester film based insulation encased in a stainless steel outer pressure vessel. A vacuum is then created between the inner and outer cylinders to reduce heat transfer into the hydrogen. The combination of low temperature and high pressure may put additional stresses on the materials used.

The shape of the storage tanks becomes an issue in vehicle applications where space is limited. Although for stress considerations, a cylindrical vessel is preferred, having a tank that could conform to a shape that fitted into naturally free space in the vehicle would be desirable from the point of vehicle design.

3.3.2 Hydrides and Carbon Nanomaterials

An alternative to gaseous or liquid storage is to store hydrogen as a solid compound. A number of metal hydrides have been used for this purpose, such as lanthanum nickel hydride ($LaNi_5H_6$), magnesium hydride (MgH_2) and sodium alanate ($NaAlH_4$). Hydrides have the advantage of very high volumetric efficiencies, i.e. a large quantity of hydrogen can be stored in a small volume, getting round the problems associated with storing hydrogen as a gas. In fact, some hydrides, such as $LaNi_5H_6$, can store more hydrogen in a given volume than liquid hydrogen. Another advantage is that this is achieved at low pressures of generally 2 – 5 bar.

The major drawback of hydrides is their weight; it would take 72 kg of $LaNi_5H_6$ to store 1 kg of hydrogen (a gravimetric efficiency of 1.4%). Other hydrides have a higher gravimetric efficiency, such as magnesium hydride (7.6%), but this hydride releases hydrogen at a high temperature. A significant amount of the energy available in the stored hydrogen must be used to generate the high temperatures. Research is needed to develop a hydride system that has a good gravimetric efficiency and good thermodynamic properties. Using hydrides in a slurry form instead of as solids is also being investigated. For slurries, instead of recharging the tank by subjecting to high pressure gas, the spent slurry would need to be pumped out and replaced by fresh slurry. The slurry would be regenerated off-board so this method would require significant additional infrastructure investment.

Another alternative is to store hydrogen in carbon nanotubes. These tubes have a very large surface area and can adsorb large amounts of hydrogen. Unlike metal hydrides, the hydrogen is not chemically bonded to the nanotubes but is held by weaker van der Waals forces. These weak forces mean a much lower temperature is needed to release the hydrogen, so the nanotubes cannot hold the hydrogen at room temperature. The release temperature can be increased to above room temperature by adding transition metals, such as titanium, which also increases the storage capacity. Currently, research into the use of nanotubes for hydrogen storage is in the early stages.

Yet another alternative is to use glass microspheres, with diameters ranging from 25 µm to 500 µm, to hold the hydrogen. When heated, the permeability of the glass increases, allowing hydrogen to pass through the wall of the sphere (typically in the order of 1 µm) into the spheres under high pressure. The spheres are then allowed to cool and the hydrogen is then trapped in the impermeable cold glass sphere. The spheres are heated again or crushed to release the hydrogen when needed. Crushing would mean that the microspheres were not reusable. As the microspheres would presumably need to be held in a container capable of withstanding the pressures needed for the storage stage, the advantages of microspheres over simple gaseous storage are not apparent.

3.4 STATIC STORAGE

For static storage the priorities are somewhat different to those of vehicle fuel tanks. Weight of the storage system is not important, and the size is less of an issue although a small footprint would still be desirable. All the technologies being investigated for vehicle fuel cells would be possible for static storage, but it is probable that liquid or compressed gas would be the most likely solutions.

The NREL report into the costs of storing and transportation of hydrogen [13] looked at a number of different methods of storing hydrogen. The most cost effective method was found to be underground storage. However, this method, which relies on a large underground cavern, would only be suitable for storage of very large volumes of gas and needs the right geological conditions. Therefore, its use would be very limited and it would not be suitable for general use at smaller sites such as at filling stations.

A set of guidelines has been written for Californian hydrogen fuelling stations [17]. The guidelines focus on refuelling vehicles that store hydrogen as a compressed gas or a cryogenic liquid, as other storage technologies (such as metal hydrides, carbon nanostructures etc. discussed in Section 3.3) are not commonly available as yet. Figure 5 shows the delivery options discussed in the guidelines and the daily dispensing capacities for which each method is appropriate. Liquid hydrogen would be pumped from the road tanker into the fuelling station storage facility. However, it is envisaged that for gaseous distribution the tube trailer would be left at the fuelling station. It would then be returned empty when the next full tube trailer was delivered. This has the advantage of low infrastructure costs for the fuelling station. An advantage of liquid storage is that the hydrogen can be dispensed as either a liquid or a gas.

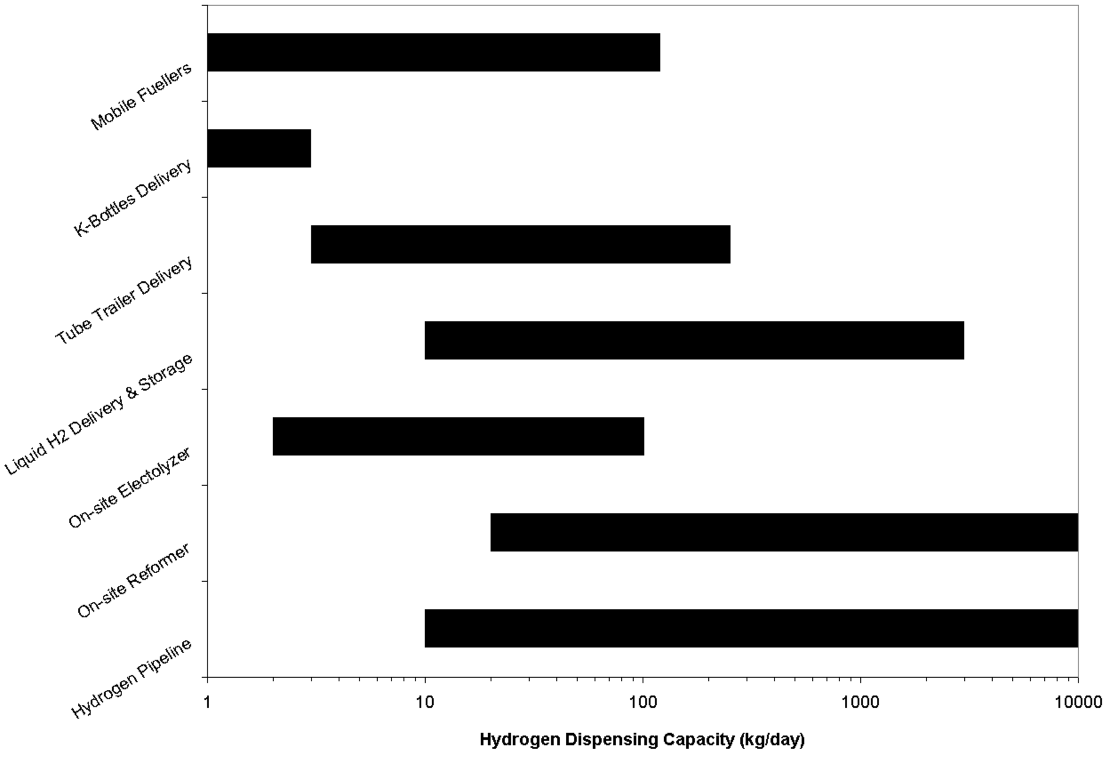


Figure 5 Range of feasible dispensing capacities from various delivery options

The final choice of which method to use for forecourt use will be, to some extent, influenced by the solution chosen for the vehicle fuel tanks. For example, if liquid hydrogen were to be stored in cars, then liquid hydrogen would have to be stored at the filling station.

3.5 HYDROGEN DISTRIBUTION

3.5.1 Tanker/Tube Trailer Distribution

Currently, the majority of hydrogen is distributed by road as either liquid in cryogenic tankers or gas in tube trailers. The relative merits of each have been discussed in Section 3.1, showing that the low capacity of tube trailers make them uneconomic for transporting hydrogen long distances.

Standard tube trailers operate at a relatively low pressure of around 20 MPa. Tube trailers are generally made up of a number of long steel cylinders connected together with a manifold. As these currently operate at a relatively low pressure, there is scope for increasing the capacity of tube trailers by increasing the gas pressure. This could be achieved by using a fibre-reinforced epoxy over-wrap on existing steel cylinders to increase the hoop strength. This could increase the pressure rating to approximately 34 MPa, with a corresponding increase in storage capacity of approximately 70%.

Transporting hydrogen as a liquid has the benefit of a larger capacity, but the costs of liquefying the gas are considerable, as the process uses approximately 30% of the total energy content of the hydrogen.

3.5.2 Pipelines

Dedicated pipelines are already in place in certain locations for transporting hydrogen. For example, Air Liquide has a pipeline network with a total length of over 800 km in France, Belgium and the Netherlands, and a smaller network in the southern United States. However, these pipelines are used primarily to transport hydrogen between specific processing plants and are not for general use. To be of use for general distribution these networks would have to be greatly extended to cover the majority of the countries involved. These pipelines, if extended, could serve regional distribution centres from where hydrogen could be distributed locally by either tube trailer or cryogenic tanker.

A major network of gas pipelines already exists across many countries to supply natural gas to homes and businesses. The possibilities of using this network to transport hydrogen gas are currently being investigated in a project called Naturalhy. This project is funded by the 6th European Framework Programme and its main objective is “Preparing for the hydrogen economy by using existing natural gas system as a catalyst”. It is a very large project, with a projected total cost of 17.2 million Euros and 39 participants, one of which is HSE. A similar project is underway in America.

Naturalhy proposes to test all the critical components of a hydrogen system by adding hydrogen to natural gas in existing networks. The concentration of hydrogen would be gradually increased. The stages are shown systematically in Figures 5 to 7, which are taken from the Naturalhy Literature Review Report [18]. There is precedent for the pipeline network carrying a mixture of hydrogen and methane; town gas that was used was a mixture containing approximately 50% hydrogen.

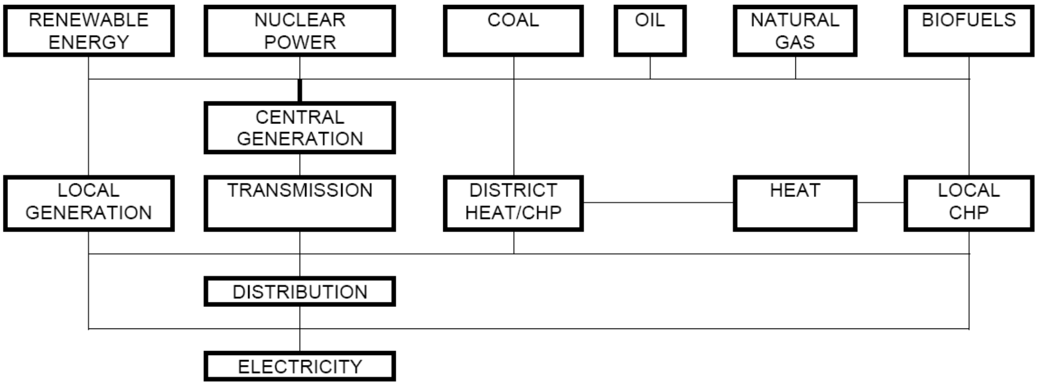


Figure 6 Current electricity systems electricity supply

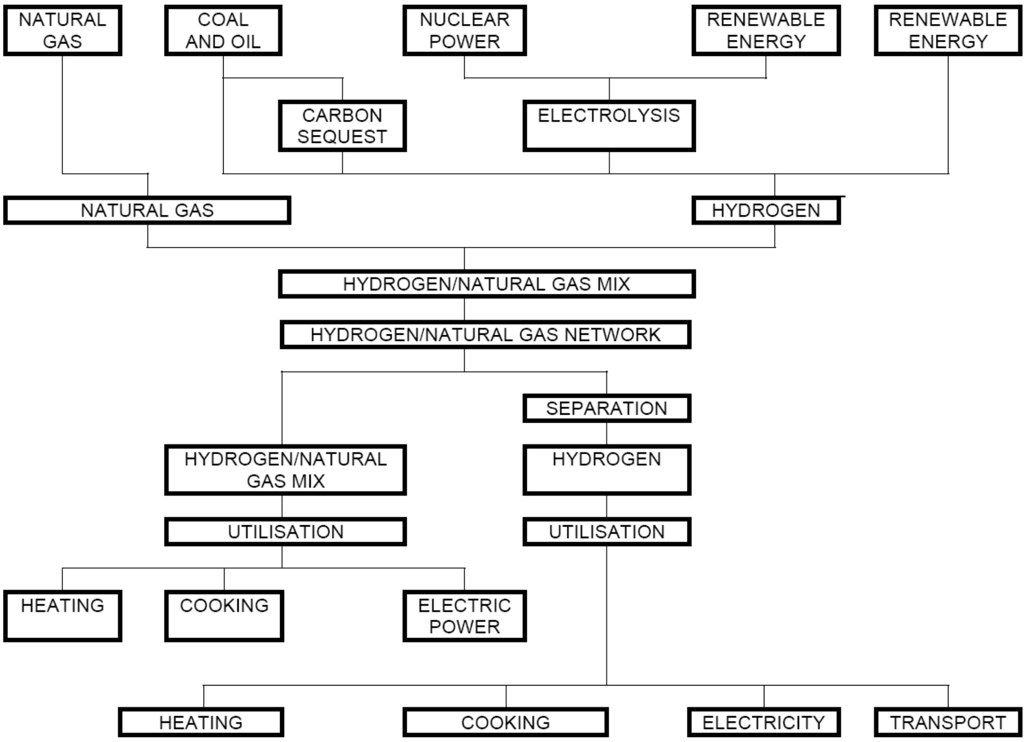


Figure 7 Transitional natural gas/hydrogen systems

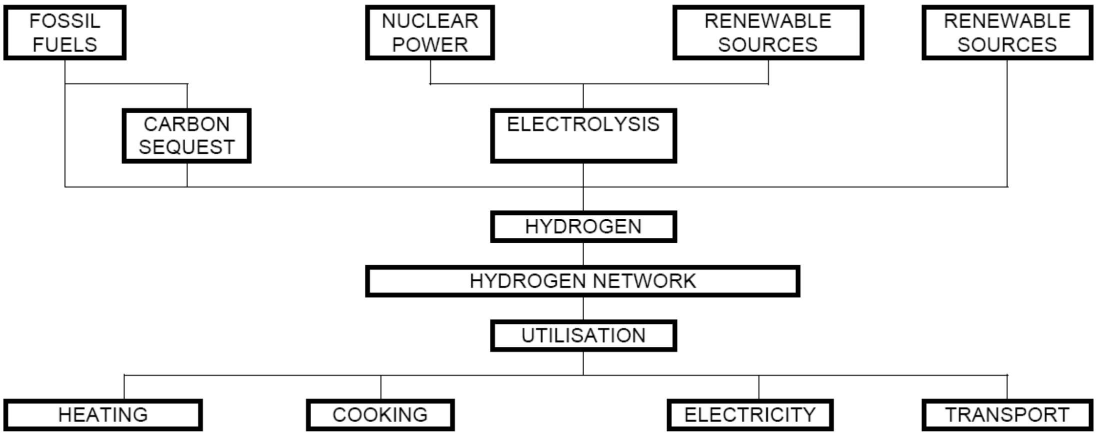


Figure 8 Future complete hydrogen system

Some people are proposing that eventually piped hydrogen will be the main source of energy for households, with the electrical needs of the home being provided by domestic fuel cells, as shown in Figure 8. However, it is difficult to conceive of a situation where it would be more economical to convert from electricity to hydrogen and back to electricity than just transmitting the electricity directly through the national grid.

One of the problems with transmitting hydrogen through pipelines is again the low energy density per unit volume of the gas, which is much lower than natural gas. Therefore, to transmit the same amount of energy, the flow rate would have to be significantly higher, meaning an increase in the gas pressure. This could cause particular problems if the existing natural gas pipeline grid was used.

A further option for pipeline distribution would be to pump liquid hydrogen in insulated pipes. The cost of laying this kind of pipeline would obviously be much higher than for a hydrogen gas pipeline, but this method could have one major advantage; adding a super-conducting wire, cooled by the liquid hydrogen, would allow electricity to be transmitted long distances without the high current losses of conventional power lines.

3.6 FUEL CELLS

There are six main types of fuel cells, and these are listed in Table 2 with their main characteristics. The alkaline fuel cell was the first fuel cell to be developed, dating back to the 1930s. It has been used in a number of applications, ranging from golf carts and tractors to the Apollo spacecraft and the Spaceshuttles. However, the very high level of purity required for this type means that it is unlikely to be used for general applications.

The phosphoric acid fuel cell (PAFC) has been the most widely used fuel cell, with many commercial units in operation. They are used for stationary power generation applications as they have an extended warm up time and low power for a given weight. Efficiencies of up to 80% can be achieved if the waste heat is used to fill other needs. The fuel cell used by Woking Borough Council for their combined heat a power system [9] is of the phosphoric acid type.

The front-runner for general use in transportation is the proton exchange membrane (PEM) fuel cell, which can either stand for proton exchange membrane or polymer electrolyte membrane. They are popular due to their high energy density and flexibility. They are also light, relatively inexpensive and durable. The US Department of Energy has identified PEM fuel cells as the preferable fuel cell for automotive, portable, residential and small commercial applications.

Although not as efficient as some other types of fuel cell, direct methanol fuel cells are gaining popularity for portable electronics devices as they operate at low temperature and have the convenience of methanol cartridges. DM fuel cells are starting to come onto the market now for laptop computers.

The high temperature fuel cells, the solid oxide (SOFC) and molten carbonate (MCFC) fuel cells, are suitable for large commercial power generation. High efficiencies of up to 85% can be achieved if the heat generated is used for heating. Because of the very high temperatures, additional electricity generation is possible if the heating effect is used to drive steam turbines. The high operating temperatures also mean that they can steam reform hydrocarbons such as methane in the fuel cell stack itself. This makes these fuel cells a viable and efficient, if expensive, alternative to the standard gas turbine electricity generation popular today. SOFCs appear to be favoured by many due to the solid electrolyte reducing the corrosion problems.

Table 2 Main types of fuel cells

Type	*Operating Temp*	*Efficiency*	*Uses*	*Notes*
PEM (Proton Exchange Membrane)	60-100°C	40% (80%)*	Transport Residential Portable	Requires expensive catalysts. Solid electrolyte reduces corrosion problems.
DMFC (Direct Methanol)	60-100°C	40%	Portable	Uses a mixture of methanol and water directly.
AFC (Alkaline)	90-100°C	60% (80%)*	Military Space	Limited usefulness due to very high level of H_2 purity needed.
PAFC (Phosphoric Acid)	175-200°C	40% (80%)*	Commercial power generation	Requires platinum catalyst. Low power/weight. Can use impure H_2 or methane.
MCFC (Molten Carbonate)	600-1000°C	55% (85%)*	Commercial power generation	Internal reformation means wide range of fuels. High temp causes durability issues.
SOFC (Solid Oxide)	600-1000°C	55% (85%)*	Commercial/ domestic power generation	Internal reformation means wide range of fuels. High temp causes durability issues.

** The percentage efficiencies in parentheses relate to fuel cells used with cogeneration, where the heat generated by the fuel cell is used for other needs such as heating*

3.7 HYDROGEN ECONOMY CONCLUSIONS

As described above there are a very wide range of applications that have been suggested for hydrogen power. If some of the more optimistic commentators are to be believed, hydrogen will be used to power all our portable electrical devices, homes, offices and transport in the coming decades.

There are many scientists and economists that have major doubts about the environmental benefits and economic feasibility of a hydrogen economy. One report [19] suggests that the problems with hydrogen production, transportation and storage are too great and suggests a synthetic-liquid-hydrocarbon economy instead. In this scenario, hydrogen taken directly from water or generated by electrolysis would be combined with carbon from biomass to generate liquid hydrocarbons, for example, methanol or ethanol, which are easier to transport and have much higher energy densities than hydrogen. Methanol could then be used in fuel cells and ethanol in internal combustion engines, possibly mixed with traditional hydrocarbons (petrol or diesel).

Another report in the magazine Scientific American [20] agrees with this hypothesis. It suggests that the lowest environmental impact in terms of overall emissions from vehicles would be for an ethanol fuel cell, where the ethanol was derived from corn. The author argues that as fuel cells work most efficiently where a low power is needed over a long period, the last place that fuel cells are likely to be found is in cars, where high power is needed quickly over short periods.

Interestingly, in his report on the limited reserves of oil and the possible actions to mitigate the effects of declining oil production, Hirsch [2] does not include the use of hydrogen as a possible solution because of the costs, service lifetimes and efficiencies of fuel cells. Major new breakthroughs, rather than just continued development, would be needed to see hydrogen as a commercially realistic option.

4 HYDROGEN CONSIDERATIONS

4.1 SPECIAL CONSIDERATIONS AND RISKS

4.1.1 Flammability

Hydrogen is flammable over a very wide range of mixtures; concentrations of hydrogen gas in air ranging from 4% to 75% are flammable. This compares to a range of 5% to 15% for natural gas and 1% to 7.8% for petrol. The minimum ignition energy is much lower for hydrogen than for other gases, at less than one tenth of the energy required for natural gas, petrol or propane. The wide range of flammable concentrations and low ignition energy are mitigated somewhat by the low density of hydrogen, which acts to disperse the hydrogen quickly.

4.1.2 Flame Arrest

The maximum experimental safe gap (MESG) – the largest gap through which an ignited fuel-air mixture will not pass – was investigated by J Hord [21]. It was found that for hydrogen, the maximum gap was 0.08 mm, whereas for methane and petrol the maximum gaps were 1.2 mm and 0.7 mm respectively, making it much harder to stop a hydrogen flame with flame arrestors.

4.1.3 Flame Colour

The flames of burning hydrogen are invisible, making fire detection more difficult. Hord [21] suggests the use of “intumescent” paints, which char, swell and emit pungent gases at low temperatures.

4.1.4 Leaks

Because of the size of the hydrogen molecules, hydrogen gas can leak more easily than other gases. Swain and Swain [22] looked at flow rates of hydrogen compared to natural gas and propane. Their main conclusion was that laminar flow, not diffusion, defines typical natural gas line leaks, and hydrogen flow rates from such leaks are only 1.26 times that of natural gas in volume rate, not the 3.8 times predicted by diffusion. Computer simulations of gas clouds in typical kitchens show that hydrogen is the least dangerous of the fuels, followed by natural gas and propane as the most dangerous.

4.1.5 Public Perception

Hydrogen has negative connotations in some people’s minds for two reasons; the Hindenburg disaster and hydrogen bombs. People are still suspicious about hydrogen. In response to news of a hydrogen filling station being build nearby, one man told his local paper “We don’t know much about it at all other than we used to make bombs out of this stuff”. Education may be needed to reassure the public of the safety of hydrogen.

4.1.6 General Safety

The general safety of hydrogen powered cars was investigated by Ford [23], comparing them to gasoline cars. The report stated that the risk of death or serious injury resulting from a gasoline fire for a 4,800 km driving trip was equivalent to working on a farm for 9 hours, or 41 seconds of rock climbing. The report concluded that the risks posed by hydrogen were generally no higher than that for a gasoline car. This was due to the strength of the high pressure cylinder, the higher rate of dispersion and the lower overall energy content of the fuel carried.

4.2 HYDROGEN SPECIFIC MATERIALS ISSUES

The NASA Safety Standard for Hydrogen and Hydrogen Systems [24] contains advice on materials for use with hydrogen systems. The document first of all notes that “awareness of the unique properties of hydrogen and the effect of cryogenic temperatures on material behaviour is essential”. It goes on to list twelve aspects to be considered when selecting materials:

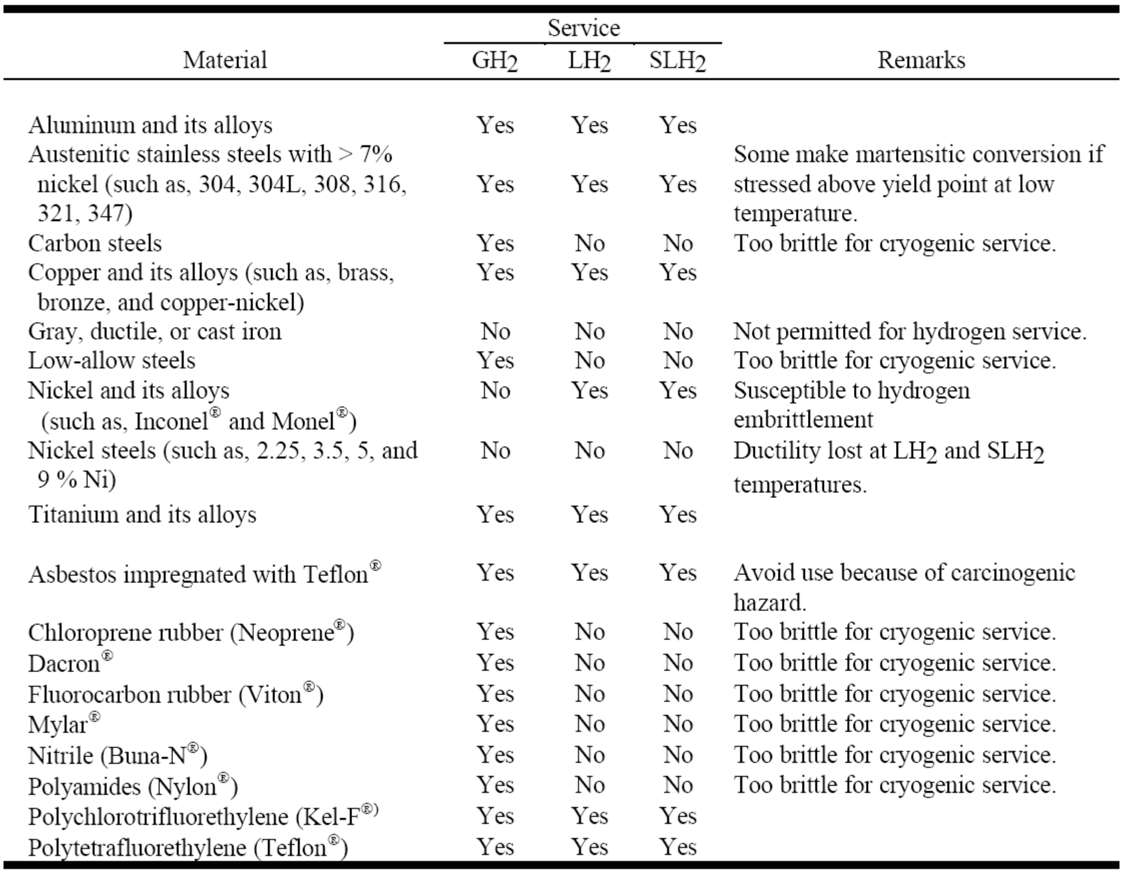
1. Properties suitable for the design and operation conditions
2. Compatibility with the operating environment
3. Availability of selected material and appropriate test data for it
4. Corrosion resistance
5. Ease of fabrication, assembly, and inspection
6. Consequences of failure
7. Toxicity
8. Hydrogen embrittlement
9. Potential for exposure to high temperature from a hydrogen fire
10. Cold embrittlement
11. Thermal contraction
12. Property changes that occur at cryogenic temperatures

Many of these considerations are applicable for any material design decision and some of them will not be appropriate for all hydrogen applications. For example, not all components will be subjected to cold temperatures.

It should be remembered that it is not just the obvious components that need to be made from an appropriate material for hydrogen use such as the pressure vessels. All the components should be considered, such as valve bodies and seats, electrical systems, insulation, gaskets, seals, tubing, lubricants and adhesives.

A more recent document covering many of the same issues has been produced for ISO [25].

Table 3 Suitability of various materials for hydrogen use (from NASA hydrogen safety standard [24])



Material	Service			Remarks
	GH_2	LH_2	SLH_2	
Aluminum and its alloys	Yes	Yes	Yes	
Austenitic stainless steels with > 7% nickel (such as, 304, 304L, 308, 316, 321, 347)	Yes	Yes	Yes	Some make martensitic conversion if stressed above yield point at low temperature.
Carbon steels	Yes	No	No	Too brittle for cryogenic service.
Copper and its alloys (such as, brass, bronze, and copper-nickel)	Yes	Yes	Yes	
Gray, ductile, or cast iron	No	No	No	Not permitted for hydrogen service.
Low-allow steels	Yes	No	No	Too brittle for cryogenic service.
Nickel and its alloys (such as, Inconel® and Monel®)	No	Yes	Yes	Susceptible to hydrogen embrittlement
Nickel steels (such as, 2.25, 3.5, 5, and 9 % Ni)	No	No	No	Ductility lost at LH_2 and SLH_2 temperatures.
Titanium and its alloys	Yes	Yes	Yes	
Asbestos impregnated with Teflon®	Yes	Yes	Yes	Avoid use because of carcinogenic hazard.
Chloroprene rubber (Neoprene®)	Yes	No	No	Too brittle for cryogenic service.
Dacron®	Yes	No	No	Too brittle for cryogenic service.
Fluorocarbon rubber (Viton®)	Yes	No	No	Too brittle for cryogenic service.
Mylar®	Yes	No	No	Too brittle for cryogenic service.
Nitrile (Buna-N®)	Yes	No	No	Too brittle for cryogenic service.
Polyamides (Nylon®)	Yes	No	No	Too brittle for cryogenic service.
Polychlorotrifluorethylene (Kel-F®)	Yes	Yes	Yes	
Polytetrafluorethylene (Teflon®)	Yes	Yes	Yes	

4.2.1 Hydrogen Embrittlement

The NASA Safety Standard for Hydrogen and Hydrogen Systems [24] contains a section on materials issues that gives information on hydrogen embrittlement. Three types of embrittlement are listed:

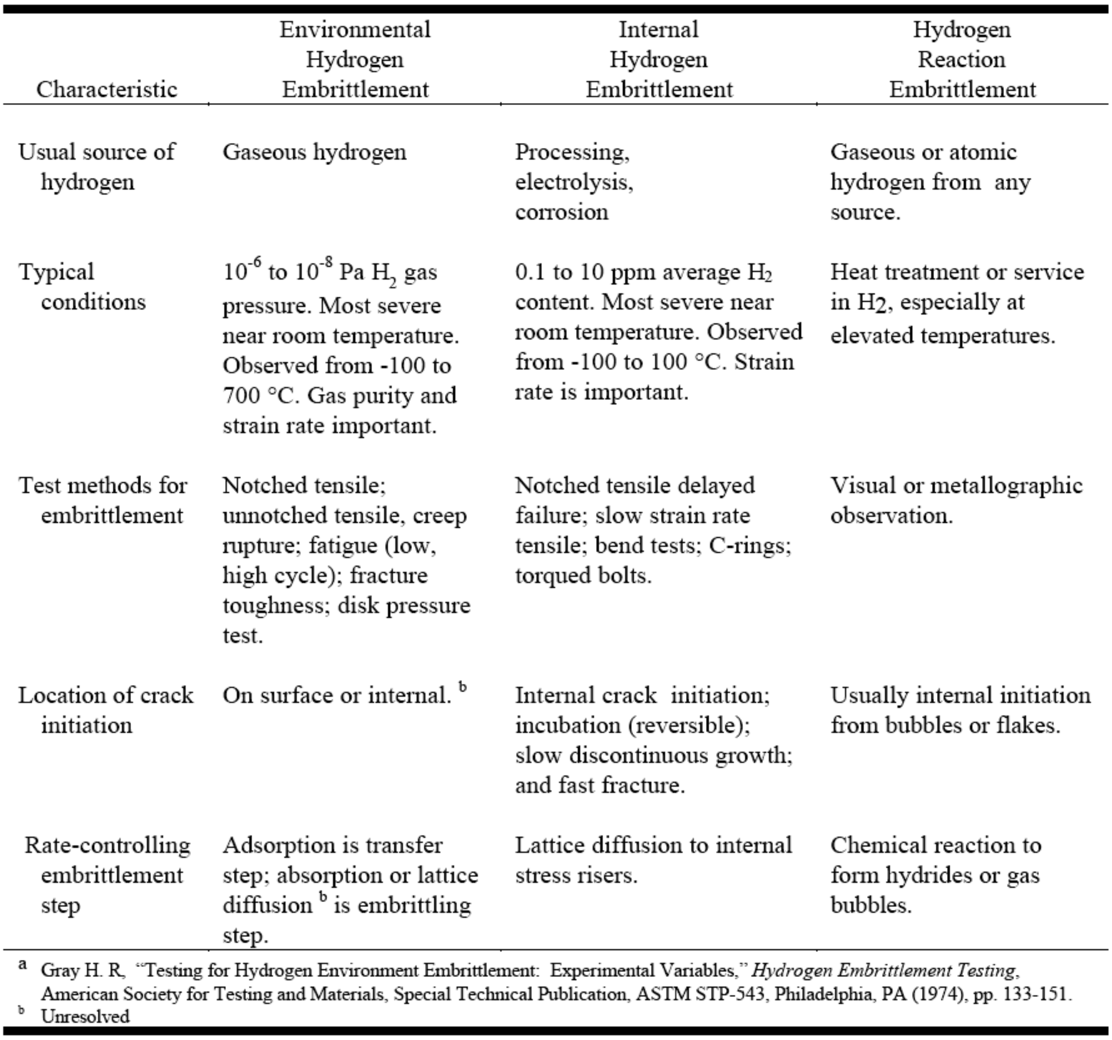
(1) Environmental hydrogen embrittlement, seen in metals that have been plastically deformed in a gaseous H_2 environment. This leads to increased surface cracks, losses in ductility and decreases in fracture stress. Cracks start at the surface.

(2) Internal hydrogen embrittlement caused by absorbed hydrogen. Failure may occur with little or no warning as cracks start internally.

(3) Hydrogen reaction embrittlement, where the hydrogen reacts with one or more of the constituents of the metal to form a brittle hydride or methane when reacting with carbon in steels.

More information about the different types of embrittlement is shown in Table 4.

Table 4 Types of hydrogen embrittlement (from NASA hydrogen safety standard [24])



Characteristic	Environmental Hydrogen Embrittlement	Internal Hydrogen Embrittlement	Hydrogen Reaction Embrittlement
Usual source of hydrogen	Gaseous hydrogen	Processing, electrolysis, corrosion	Gaseous or atomic hydrogen from any source.
Typical conditions	10^{-6} to 10^{-8} Pa H_2 gas pressure. Most severe near room temperature. Observed from -100 to 700 °C. Gas purity and strain rate important.	0.1 to 10 ppm average H_2 content. Most severe near room temperature. Observed from -100 to 100 °C. Strain rate is important.	Heat treatment or service in H_2, especially at elevated temperatures.
Test methods for embrittlement	Notched tensile; unnotched tensile, creep rupture; fatigue (low, high cycle); fracture toughness; disk pressure test.	Notched tensile delayed failure; slow strain rate tensile; bend tests; C-rings; torqued bolts.	Visual or metallographic observation.
Location of crack initiation	On surface or internal. [b]	Internal crack initiation; incubation (reversible); slow discontinuous growth; and fast fracture.	Usually internal initiation from bubbles or flakes.
Rate-controlling embrittlement step	Adsorption is transfer step; absorption or lattice diffusion [b] is embrittling step.	Lattice diffusion to internal stress risers.	Chemical reaction to form hydrides or gas bubbles.

[a] Gray H. R, "Testing for Hydrogen Environment Embrittlement: Experimental Variables," *Hydrogen Embrittlement Testing*, American Society for Testing and Materials, Special Technical Publication, ASTM STP-543, Philadelphia, PA (1974), pp. 133-151.

[b] Unresolved

The susceptibility of metals to hydrogen embrittlement varies greatly from metal to metal. For example, the strength of a notch specimen of 18Ni-250 Maraging Steel in H_2 at 10,000 psi (69MPa) is only 12% of the strength of a similar specimen tested in a helium environment. However, 310 Stainless Steel maintains 93% of its strength in a hydrogen environment (Chandler and Walter [26].) The effect of different alloying elements has been described by Thompson and Bernstein [27], and these are shown in Table 5.

Table 5 Effect of various alloying elements on susceptibility to hydrogen embrittlement

Alloying Element	*General Susceptibility*
Manganese	Increases
Sulphur and Phosphorus	Appears to increase
Carbon (in carbon marensites)	Appears to increase
Chromium	Increases
Titanium	Reduces
Titanium in Maraging Steels	Increases
Silicon	Reduces
Molybdenum	No consistent behaviour
Nickel	Not known
Tungsten	Not known
Vanadium	Not known

Operating temperature also has an effect on the level of embrittlement. For many metal, the effect of internal and environmental embrittlement is most severe at low temperatures, between 200 and 300 K [28]. However, hydrogen reaction embrittlement is associated with higher temperatures, above room temperature.

The effect of hydrogen embrittlement is generally greater as the purity of the hydrogen increases, and as the level of tensile stress increases.

The ISO technical report 15916 [25] lists a number of ways that susceptibility to hydrogen embrittlement can be reduced:

- Restricting the hardness, and therefore the strength level of the material used, to a safe value
- Lowering the level of applied stress
- Minimising residual stresses, for example by stress-relieving weldments and by normalising or fully annealing cold-worked materials
- Avoiding situations that can lead to local fatigue in components that are subjected to frequent load cycles, since hydrogen is known to significantly accelerate a possible initiation and propagation of fatigue cracks in a structure
- Using austenitic stainless steels, which in general are less susceptible to hydrogen embrittlement and are commonly used as structural materials for hydrogen equipment because of their excellent toughness behaviour at cryogenic temperatures
- Using the test methods specified in ISO 11114-4 to select metallic material resistant to hydrogen embrittlement

4.2.2 Cryogenic Operating Temperatures

Because of the low density of hydrogen gas, a large volume is needed to provide the necessary energy requirements. One way of reducing the volume substantially is to liquefy the hydrogen. The boiling point of hydrogen at atmospheric pressure is just 20 K. At higher pressure this can increase to a maximum temperature of 33 K (the critical temperature). The critical pressure is 1.3 MPa so there is no advantage in terms of boiling point in increasing the pressure above this level. The very low temperature at which liquid hydrogen is stored has implications for the material properties of the materials used.

Generally, materials are more brittle at low temperatures, with some materials having a sudden transition from ductile to brittle at a certain temperature, such as carbon steels and 201 stainless steel, as shown in Figure 9. However, others, such as 304 stainless steel, actually have slightly improved toughness at low temperature. Generally, the tensile and yield stresses of materials increase at low temperature.

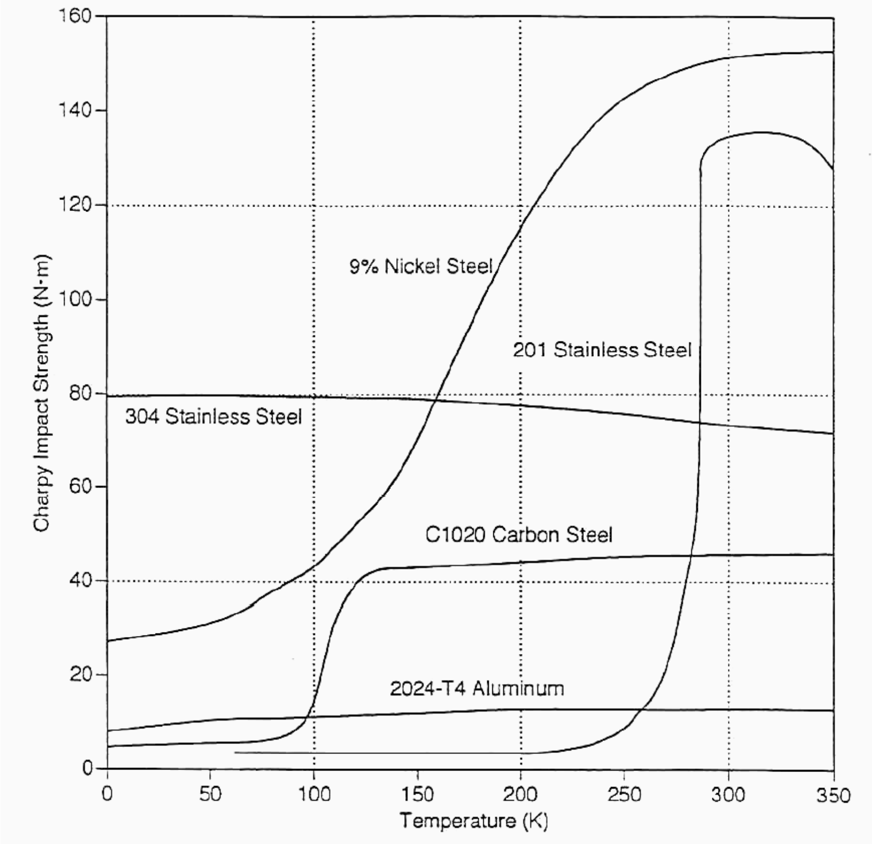


Figure 9 Effect of temperature on Charpy impact strength for a range of metals (NASA H_2 Safety document [24], originally from Brown *et al* [29] and Durham *et al* [30])

Material selection for use with liquid hydrogen must be carefully considered and it should be remembered that the components would probably be operating at higher temperatures for some of the time.

4.2.3 High Pressure Containers

Another option for increasing the density of the hydrogen is to store it under high pressure. This is a less energy intensive alternative to liquefying the gas, which uses approximately 30% of the energy content of the hydrogen.

There are basically four different types of container for high pressure gas storage;

- Type 1 – Seamless metallic container
- Type 2 – Hoop wrapped container with a seamless metallic liner
- Type 3 – Fully wrapped container with a seamless or welded metallic liner
- Type 4 – Fully wrapped container with a non-metallic liner

For transporting hydrogen gas tube trailers are used, generally operating at a pressure of 20 MPa. These are of type 1, although they could be converted to type 2 by using a fibre-reinforced epoxy over-wrap to increase the hoop strength. This could increase their pressure rating to approximately 34 MPa, increasing the storage capacity by over 70%.

An alternative to storing hydrogen as a liquid is to store it as a gas at high pressure. The higher the pressure, the more hydrogen can be stored in a given volume, therefore the greater the range of vehicles, etc. Quantum Technologies currently has the highest pressure vessel, rated at 10,000 psi (70 MPa). The construction of the cylinder is based on their Trishield ™ technology, which consists of a polymer lining, a carbon reinforced composite material and an outer protective coating. The role of the polymer lining is to prevent the hydrogen affecting the main composite component. It is the composite cylinder that takes the stress of the high pressure gas. The outer coating is to protect the main cylinder from external damage.

The composite used for the main structural layer of the cylinder is too expensive for the cylinder to be able to meet the US Department of Energy cost targets. Therefore, Quantum are looking into using a cheaper composite with a lower carbon fraction to reduce costs. This would ultimately reduce the strength of the cylinder and therefore reduce the safety factor. To compensate for this, Quantum are looking into ways to increase the safety of the cylinder in other ways, by using condition monitoring systems such as acoustic emissions.

Pressure vessels must undergo a rigorous set of tests before being approved. These tests include drop tests, fire tests, bullet tests and corrosion tests. The full range of tests in the draft European regulations is discussed in Section 6.2.

4.2.4 Storage Media

The use of storage media, such as metal hydrides and carbon nanotubes means that large quantities of hydrogen can be stored without the need for high pressure or cryogenic temperatures. Therefore, the materials implications for the vessels are less than for other methods of storage. However, the storage media may present some safety implications. For example, in order to increase the surface area, metal hydrides are typically used in powder form, which may be highly flammable if dispersed in air. A literature review was conducted in 2004 by HSL on the explosion hazards associated with nanopowders [31]. One of the main conclusions was that although there was a considerable body of knowledge on the explosion characteristics of micron-scale powders (10 to 500 µm particle size), there was no data for nanopowders (particle sizes from 1 to 100 µm).

There may also be toxicology issues related to breathing in fine particles and nanotubes. At present, there are many questions about the possible health issues surrounding these materials and more work must be done to answer these questions. However, these issues are only relevant if the media escape from the storage vessel.

4.2.5 Pipelines

There are three potential problems with the use of pipelines for the distribution of hydrogen. Firstly, the low energy density requires the pipelines to operate at a higher pressure in order to offer suitable economics. Secondly, hydrogen is prone to leak readily through very small gaps and to permeate through some materials. The third potential problem is the effect of hydrogen on the materials themselves, mainly hydrogen embrittlement of metals. Using existing natural gas pipelines would encounter additional problems related to the separation of hydrogen from the natural gas, or the conversion of all the gas appliances connected to the pipeline.

A number of approaches are being developed to counter the material problems involved. These include developing a plastic pipe with an embedded aluminium lining to reduce permeation losses. An alternative would be to coat steel pipelines with an impermeable barrier.

4.2.6 Fuel Cells

There are material safety issues relating to fuel cells. The range of different electrolytes used in the different types of fuel cells gives rise to different concerns. For some, such as the molten carbonate fuel cell, the main concern would be over the safety of the electrolyte itself, as this would be damaging to health if not contained properly. This type of fuel cell is likely to be used for static applications only, so the chances of impact damage resulting in a release would be low.

The durability of the solid membranes is at present limited, with a lot of research effort being directed to increase the lifetime. How the membranes fail could have serious safety implications if the failure results in the possibility of hydrogen mixing with air.

5 REGULATIONS AND ENFORCEMENT

In parallel with the research and development into hydrogen production, distribution and use, considerable effort is being expended in the area of standards and enforcement. Some of the recent standards applicable to hydrogen storage, although not specifically for hydrogen, are BS EN 12245:2002 [32], BS EN 12257:2002 [33], ISO 11119-x:2002 [34-36] for composite cylinders. The ISO 11119 standard “Gas cylinders of composite construction – Specifications and test methods” is in three parts; Part 1: Hoop wrapped composite gas cylinders, Part 2: Fully wrapped fibre reinforced composite gas cylinders with load-sharing metal liners and Part 3: Fully wrapped fibre reinforced composite gas cylinders with non-load-sharing metallic or non-metallic liners. All parts are applicable to cylinders with a water volume of up to 450 litres and a maximum test pressure of 650 bar.

The British Standards, BS EN 12245:2002 and BS EN 122257:2002 cover transportable gas cylinders of fully wrapped composite and seamless, hoop-wrapped composite designs respectively. These standards specify the minimum requirements for the materials, design, construction, prototype testing and routine manufacturing inspections of composite gas cylinders of up to 450 litres capacity. Unlike the ISO standards, a upper limit on the maximum test pressure of the cylinders is not specified.

These standards are general and not specifically for hydrogen use. The draft ECE Compressed Gaseous Hydrogen Regulation document [37] is specific to hydrogen application, but contains many of the same types of tests as the BS EN standards. There is a requirement for the cylinders to be compatible with their contents, specified in the ISO/DIS 11114 standards [38].

Two draft standards are looked at in detail here to see the types of tests that might be required in the future.

5.1 DRAFT ECE COMPRESSED GASEOUS HYDROGEN REGULATION

This draft document [37] was prepared by UN ECE WP.29 GPRE Informal Group “Hydrogen/Fuel Cell Vehicles” based on proposals originally developed by the Partners of the European Hydrogen Project – Phase II (EIHP2). The regulations define four different types of container:

- Type 1 – Seamless metallic container
- Type 2 – Hoop wrapped container with a seamless metallic liner
- Type 3 – Fully wrapped container with a seamless or welded metallic liner
- Type 4 – Fully wrapped container with a non-metallic liner

Different test are applicable to different types of container, as shown in Table 6. More details about the different tests are given in Section 6.2.

Table 6 Types of test described by draft ECE Regulations

Test No	*Test*	*Applicability*	*Description/Standard*
B1	Tensile Test	4 - liner only	Tensile test at -40ºC (ISO 527-2)
B2	Softening/Melting Temperature test	4 - liner only	A50 method in ISO 306
B3	Glass Transition Temperature test	2,3,4 resin material	ASTM D3418
B4	Resin Shear Strength test	2,3,4 resin material	ASTM D2344
B5	Coating Test	1,2,3,4	Depends on type of coating
B6	Coating batch test	1,2,3,4	ISO 2808 ISO 4624
B7	Hydrogen compatibility test	1,2,3	Own test method unless satisfies other standard
B8	Hardness test	1,2,3 metallic materials	ISO 6506-1
B9	Burst test	1,2,3,4	Own test method
B10	Ambient temp pressure cycling test	1,2,3,4	Own test method
B11	LBB Performance test	1,2,3,4	Own test method
B12	Bonfire test	1,2,3,4	Own test method
B13	Penetration test	1,2,3,4	Own test method
B14	Chemical exposure test	2,3,4	Own test method
B15	Composite flaw test	2,3,4	Own test method
B16	Accelerated stress rupture test	2,3,4	Own test method
B17	Extreme temperature pressure cycling test	2,3,4	Own test method
B18	Impact damage test	3,4	Own test method
B19	Leak test	4	Own test method
B20	Permeation test	4	Own test method
B21	Boss torque test	4	Own test method
B22	Hydrogen gas cycling test	4	Own test method
B23	Hydraulic test	1,2,3,4	Own test method

5.2 ISO/DIS 11114-4 CAPABILITY OF CYLINDER AND VALVE MATERIALS WITH GAS CONTENTS PART 4: TEST METHODS FOR SELECTING METALLIC MATERIALS RESISTANT TO HYDROGEN EMBRITTLEMENT

The standard is currently a draft for public comment [38] so some of the details listed below are liable to change. The proposed standard contains three types of test;

1. Method A, Disc Test
2. Method B, Fracture mechanic test
3. Method C, Test method to determine the resistance to hydrogen assisted cracking of steel cylinders

It is envisaged that the final standard will contain Method A and either Method B or Method C, but not both.

5.2.1 Method A, Disc Test

This method determines the extent of hydrogen embrittlement by subjecting a thin disc to increasing pressures using hydrogen and helium until the disc ruptures. The ratio of the two rupture pressures gives a measure of the level of embrittlement.

The dimensions of the disc are set as a diameter of 58 mm and a thickness of 0.75 mm, and flatness and roughness are controlled. The discs are mounted in special apparatus and pressurised using hydrogen or helium at a range of pressure rise rates. The ratio of helium rupture pressure to hydrogen rupture pressure is calculated and the maximum ratio obtained is the embrittlement index. The material would be considered suitable for compressed hydrogen cylinders if the index was less than, or equal to, 2.

5.2.2 Method B, Fracture mechanic test

This test determines the threshold stress intensity factor (K_{1H}) for susceptibility to cracking of metallic materials in gaseous hydrogen. The procedure covers the use of machined compact tension test pieces, as described in ISO 7539-6, for the determination of the threshold stress intensity factor, as described in ISO 7539-1.

The specimens for test are compact tension specimens, according to the geometry set out in ISO 7596-6, with a W dimension of 26 mm and a thickness equal to the greatest thickness allowed by the cylinder wall curvature and thickness, but not less than 85% of the design thickness of the cylinder. The specimen is pre-cracked in air.

The test itself is carried out at a pressure of 150 bar, with hydrogen of at least 99.9995 % purity. The test starts at a load that produces a stress intensity factor of 1 MPa√m, or 50 % of the stress intensity factor obtained from any previous work that might have been done. The specimen is held at this load for 20 minutes. Assuming no crack growth is detected, the load is increased so that the stress intensity factor at the crack tip is increased by 1 MPa√m and held for a further 20 minutes. This procedure is repeated until failure occurs.

The threshold stress intensity factor is calculated:

$$K_{1H} = YP/BW^{1/2}$$

where Y is the geometric correction factor, P is the load applied to the specimen before the final increment that caused failure, B is the thickness and W is the effective width of the specimen. The criteria for acceptance is that both the values of K_{1H} obtained for the two tests are greater than or equal to 60/950 × R_m, where R_m is the average of the tensile strength values obtained from two tensile tests.

5.2.3 Method C, resistance to hydrogen assisted cracking

In this method, instead of increasing the stress intensity factor until failure occurs, the stress intensity factor is held at a set level for a set time. The crack growth is then measured to determine whether any significant hydrogen assisted cracking has occurred.

The specimens to be tested are the same as those for method B, with the same geometry and pre-cracking. The specimens are loaded in a hydrogen environment by either constant load or constant displacement, for at least 1000 hours. The loading is set to produce a stress intensity factor at the crack tip equal to 60/950 × R_m, which is the same as the pass level for method B. After the test, the specimen is unloaded and the hydrogen assisted cracking is marked by heat tinting, fatigue beach marking or fracturing the specimen at a very low temperature. The crack growth is then measured using a scanning electron microscope and if the growth is less than 0.25 mm, the specimen passes the test.

6 CONCLUSIONS

1. Hydrogen is seen by many as the answer to the environmental problems of reliance on fossil fuels for energy needs. A great deal of effort is currently being invested in research into all areas of the hydrogen economy, such as fuel cells, hydrogen generation, transportation and storage.

2. Fuel cells have the potential to provide power for a very wide range of applications, ranging from small portable electronics devices to large stationary electricity production and vehicles covering the whole range of road vehicles and possible extending to rail, marine and even aviation.

3. The main obstacles to achieving a viable hydrogen economy are costs of producing hydrogen from renewable sources, issues relating to transportation and storage due to the low energy density of hydrogen gas, and the cost and reliability of fuel cells.

4. The main material considerations relating to the use of hydrogen are hydrogen embrittlement, material properties at cryogenic temperatures (due to use of liquid hydrogen) and permeability.

5. A number of new materials are likely to come to prominence in a hydrogen economy; High performance composites are likely to be used extensively for high pressure hydrogen cylinders. New materials, or combinations of materials, may be used for hydrogen pipelines. A range of new materials are currently being considered for hydrogen storage, such as metal hydrides and carbon nanotubes.

6. Due to the effect of hydrogen on materials, it is important to test any materials in the environment in which they would be used. Depending on the type of test, this could require the use of very specialist, expensive equipment.

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