

1

Introduction

1.1

History/Background

Storage of hydrogen is still one of the key issues of the usage of hydrogen itself for vehicle transportation. Main activities on these fields were recorded in the early times of space flight, whereas launching-systems/liquid propelled systems were driven by hydrogen and oxygen fuel.

The development of lightweight tank systems played – from the beginning – a very important role [1], as well as the adjusted issues of pipes, hoses, and dressings.

In Figure 1.1 a typical setup of a pressurized hydrogen or oxygen tank is given, designed with a filament winding method from the early 1950s and 1960s of the last century.

From these issues the storage of hydrogen can be mainly divided into two major technology approaches:

- Pressure storage, CH_2 , using high pressurized H_2 in special tank systems in order to store an amount of n-kg of mass for the use in vehicles.
- Liquid storage, LH_2 , where the gaseous agent is liquefied below 50 K with moderate pressure (less than 10 bar) and held in a thermo-insulated tank setup.

In this chapter the emphasis will lie on the background of pressurized storage of hydrogen with a special focus on ground transportation, automotive, and tracking.

In Figure 1.2 the basic storage capacities of LH_2 and CH_2 are given with respect to cost and manufacturability margins.

The early developments of hydrogen tanks are closely linked with space flight programs such as Mercury, Gemini, Delta, and the Apollo program, only to mention NASA projects.

The demands of space flights as a part of early application in transportation are very high, on the other hand cost and manufacturing issues played a minor role in this field of application. Due to technical boundary conditions, mainly cylinder- or elliptical-cylinder-tanks were designed which were the best fit for the fuselage of launchers. This layout was mainly driven by static determinations of the current

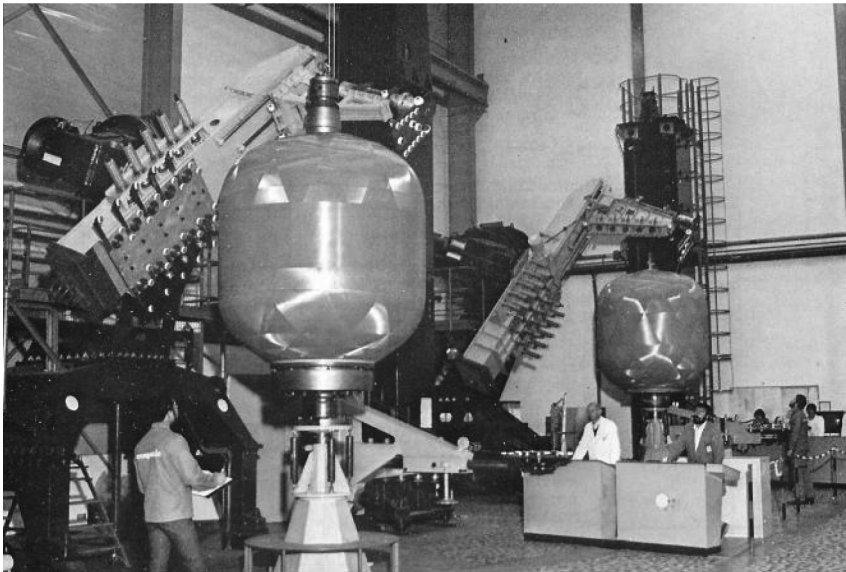


Figure 1.1 H₂ and O₂ tanks manufactured with filament winding technique in Lockheed–Martin laboratories.

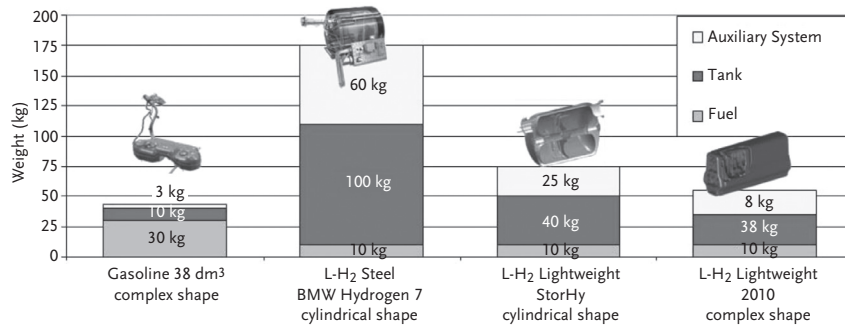


Figure 1.2 CH₄ and LH₂ storage outlines with respect to design, cost, and weight margins.

limited ultimate load-cases where the burst and rupture strength of the structure were taken into account for layout. In addition to that, dressing systems were mainly driving the weight-penalty of the structure, by demanding special in- and out-design-features as an interface to composite materials.

Figure 1.3 explains the problem field of interfaces and connectors between dressing-systems and the homogeneous and monolithic tank structure.

The usage of tank systems for ground transportation or vehicles had already been introduced in the early 19th century within the use of hydrogen carriages. Figure 1.4 shows the earliest hydrogen application ever recorded on a carriage system by De Rivaz from 1808.

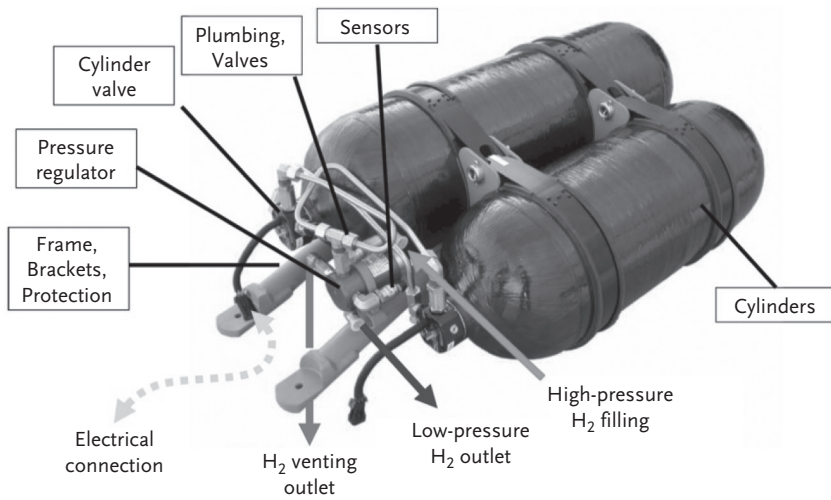


Figure 1.3 Problem field of interconnection between dressings and the monolithic composite.

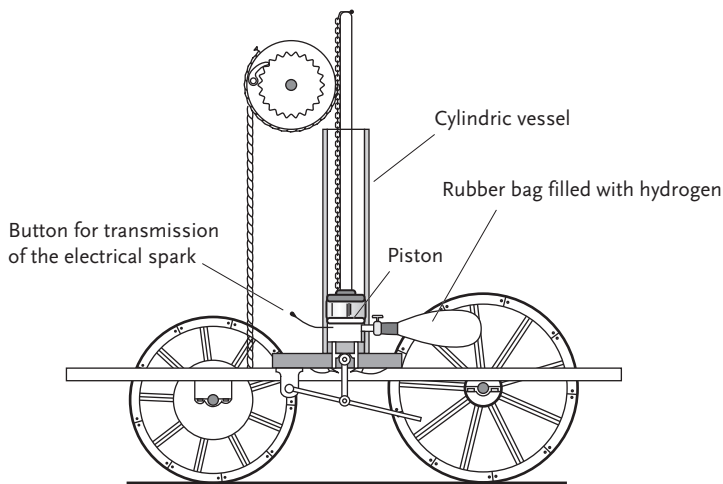


Figure 1.4 The earliest application of hydrogen in a ground transportation vehicle – carriage – the earliest predecessor of cars.

The development of tank systems for automotive application in the second half of the last century was mainly driven by BMW automotive tank systems, which were using internal combustion engines (ICEs) as the main propulsion system (Figure 1.5). This project, among other parallel developments such as Ford, Man, Mazda, see [2], was one of the main drivers of hydrogen storage, as well as this, BMW has decided to use the storage system LH₂ from the very beginning in order to carry more kilograms of hydrogen and therefore to extend the range.

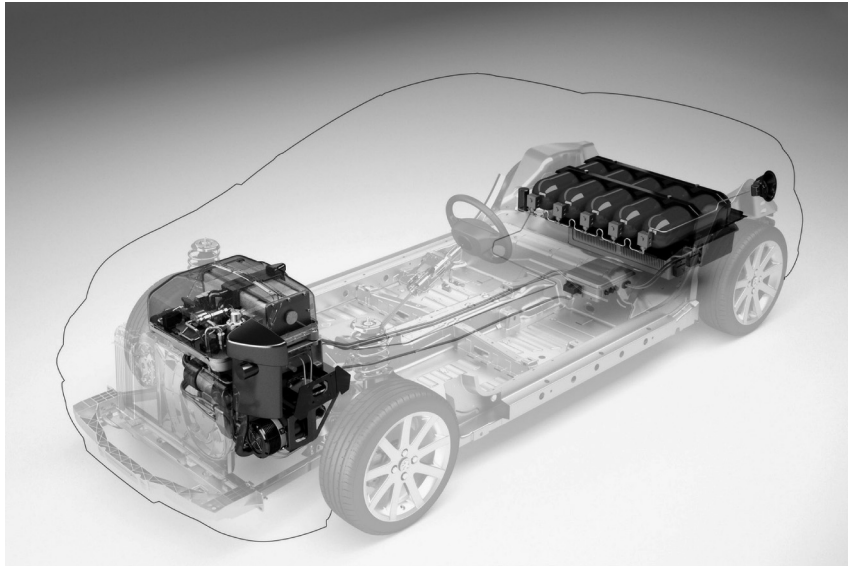


Figure 1.5 Tank system with the use of CH_2 for PSA automotive application using a cylindrical tank rack system in a conventional passenger car.

The recent projects founded by the European government – mainly StorHy (2004–2008) – were focused on the cost critical and production critical issues of the storage of hydrogen and have also lined out major criteria for a practical use of hydrogen in passenger car vehicles.

In [3], a brief overlook at the results of the StorHy project is given, the main aspects of the developments of this project are also used by the authors as an input for future strategies of hydrogen storage.

1.2

Tanks and Storage

The storage of a gaseous agent in tank systems under pressure or high pressure can be linked to the conventional task of layout of pressurized vessels in engineering mechanics.

Mainly the gas, as the fuel for the propulsion system, will be put under high pressure and stored in mostly rotationally symmetric tank systems. The pressure especially for hydrogen will vary between 100 and 750 bar, in particular driven by the demand of the vehicle. This pressure range allows between 0.5 and 3 kg of H_2 to be carried. Figure 1.6 shows a conventional tank system by the manufacturer Dynetek with the daily operational pressure of 350 bar and the burst pressure of about 1000 bar.



Figure 1.6 Conventional CH₂ pressurized tank system for automotive usage at 350 bar.

This tank is designed with an aluminum liner on the inside to avoid critical H₂ permeation and a filament wound carbon fiber hull is used to cope with the high circumferential stresses.

With a storage mass of about 1 kg of hydrogen a typical range of about 100 km can be reached using an internal combustion engine (ICE) and about 150 km on conventional fuel cell applications (F/C). This would automatically demand a typical required mass of at least 3 kg hydrogen for a passenger car, in order to establish practical useful ranges for the customer.

Pressurized gas in tank systems will lead to high circumferential normal stresses, which can be calculated using the pressure-vessel theory. Pressure vessels based on a rotationally symmetric topology can be calculated with the so-called half membrane theory, which will include the membrane stress state and a set of transfer forces for the static equilibrium balance. The normal forces and the shear stresses can be calculated as a function of the metric of the tank system with the conventional orthotropic shell theory [4].

In Figure 1.7 the stresses are shown as a function of the cutting reactional forces of the shell under internal pressure load.

With the help of the statical determination by balancing all forces and moments, the main stresses of the vessel under internal pressure load can be calculated. The investigation of this phenomenon shows that all designed tank systems following this strategy would be inwardly statically determined, whereas the determined stresses are only a function of metric and wall thickness.

If the loads of the shell mid place are described by the load vector

$$\mathbf{q} = q^\alpha \mathbf{a}_\alpha + q^3 \mathbf{a}_3$$

that is relating to their unit of area, the membrane equilibrium state of the shell element follows – under the condition of neglected shear forces $Q^\alpha = 0$ – to

$$N^{\alpha\beta}|_\alpha + q^\beta = 0$$

$$N^{\alpha\beta} b_{\alpha\beta} + q^3 = 0$$

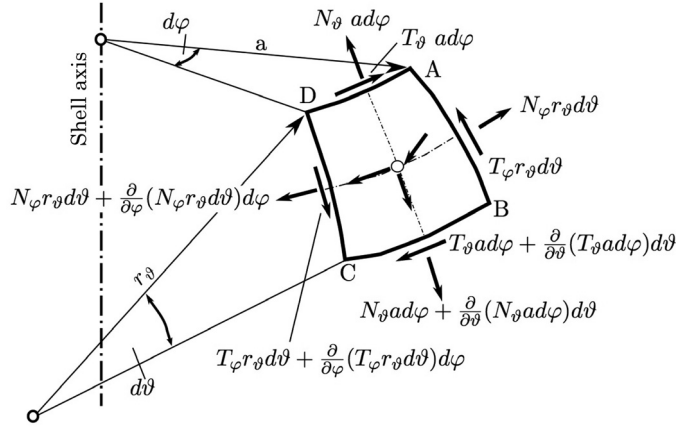


Figure 1.7 Cutting reactional forces of a shell element under internal pressure.

The partial derivative of the covariant basis vectors

$$\mathbf{a}_{\alpha,\beta} = \frac{\partial \mathbf{a}_\alpha}{\partial \Theta^\beta} = \Gamma^\rho_{\alpha\beta} \mathbf{a}_\rho + \Gamma^3_{\alpha\beta} \mathbf{a}_3$$

is here reflected in the covariant derivative $n^{\alpha\beta}|_{|\alpha}$. The term

$$\Gamma^3_{\alpha\beta} \mathbf{a}_3 = \mathbf{a}_{\alpha,\beta} \cdot \mathbf{a}_3$$

results in the consideration of the curvature in the equilibrium of forces in normal direction. Further deduction leads to the balance of forces in component notation

$$\overline{N}^{\alpha\beta}|_{|\alpha} + \overline{q}^\beta = 0$$

$$\overline{N}^{\alpha\beta} x^3|_{|\alpha\beta} + \overline{N}^{\alpha\beta}|_{|\alpha} x^3|_{|\beta} + \overline{q}^3 = 0$$

Showing the main circumferential stresses as a function of pR/t the layout of the vessel system can mainly be focused on this simple formula. Following the metric of cylinder/paraboloid shells versus spherical shells the critical stresses in spheres are only half of the main axial stresses in the other shells.

Because of the character of spherical shells storage, the advantage of this geometry is not only in stresses but also in having a high mass of hydrogen in a very limited amount of space which means the smallest room. This was the reason why spherical shells were mainly used for space-flight applications as well as for submarine and sea-vessel usages.

The complexity of the dressing system and the necessity of putting in and out hoses and wirings lead to so-called edge-design, which can cause the introduction of sharp bending cutting reactional bending moment gradients. Figure 1.8 shows a typical peak-stress environment on a conventional tank system filled with a liquid source.

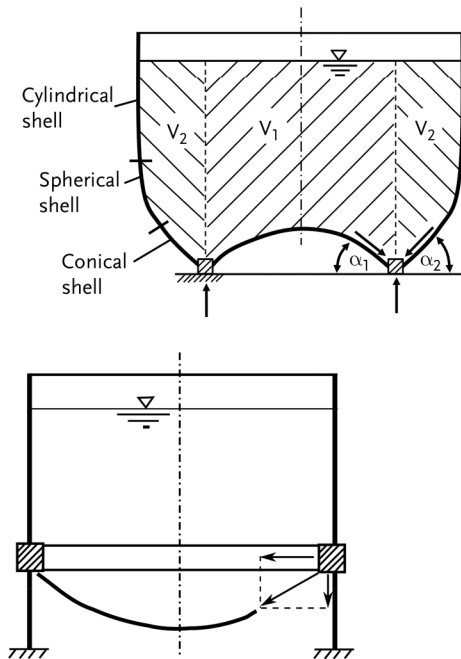


Figure 1.8 Typical bending moment peak-gradient on the transition phase between the cylinder and bottom wall.

With the calculation of the main-stress-state of the tank system, the strength of the structure can be derived mainly by using conventional failure criteria, as shown by Von Mises and Tresca. Using these criteria would lead to the insight that – for the fatigue loading of tanks with storage pressure of more than 200 bar – a conventional steel design is no longer feasible. The yield strength of modern steel alloys, even for multiphase steels lies in a region of 700–1100 MPa.

Comparing the strength allowable with the calculated main stresses, low or negative margins of safety for homogeneous monolithic tanks using isotropic materials is shown. In order to gain the required strength of the to-be-designed tank structure monolithic materials such as steel or aluminum alloys on a sheet metal base are no longer sufficient. High stresses due to internal pressure loading up to 750 bar require the usage of new fiber material such as carbon or polyamide fibers. This requirement leads to the introduction of high tensile carbon fibers, which can provide strength values up to 2000–3000 MPa. In addition to that, low rupture strain characteristics of the fibers will lead to a reliable layout of the new tank generation. The combination of carbon fiber with resin material such as epoxy or PUR will lead to a new generation of carbon fiber reinforced plastics (CFRP).

In Table 1.1 the basic material properties of new fiber generations are given. It is clearly visible that only carbon or PA fibers can cope with the demand of high circumferential daily fatigue stresses of the hydrogen tank.

Table 1.1 Tensile strength values and Young's moduli of modern fiber generations.

Fiber	Density (g cm ⁻³)	Young's modulus (longitudinal) (GPa)	Tensile strength (MPa)	Elongation at fracture (%)	Coefficient of thermal expansion (10 ⁶ °C ⁻¹)
Carbon	1.74–1.81	230–800	2150–4500	0.4–2.1	–1.1––0.5
Glass	2.14–2.54	55–90	1650–4500	3.0–4.0	3.5–7.2
Aramid	1.44	135–185	2800–3500	2.1–4.3	–2
Basalt	2.65–2.75	89–100	3000–4800	3.2	–
Zylon [®] (PBO)	1.55	180–270	5800	2.5–3.5	–6
Dyneema [®] (PE)	0.97	89–172	2700–3600	3.6	–12.1
Innegra [®] (PA)	0.84	18	590	7.2–8.6	–
Vectran [®]	1.40	103	1100–3200	3.3	–
Natural	1.00–1.50	22–55	390–700	–	–
Silicon carbide	2.55	176–400	2450–2950	0.6–1.9	3.1
Quartz	2.20	78	3300–3700	–	0.5
Aluminum oxide	2.70–3.90	150–380	1700–3100	0.6–1.1	3–8

CFRP with thermoset resin systems would have high permeation rates for hydrogen molecules. These values lay more than 10³ times higher than conventional metal alloys such as aluminum or steel. For this reason an inner- or outer-lining system has to be introduced in order to minimize the leakage rate. Such lining systems are mainly used for ground transportation or car usages and will be produced by 3D-rollforming. The aluminum vessel can be used as a mold for filament winding processes or tape-layup CFRP production techniques. Following that the carbon fiber reinforcement will strengthen the aluminum liner to provide high rupture strength in the matter of a circumferential wrapped filament. The permeation rate of aluminum sheet metal is very low, so aluminum is a favorite material for any containment issues for hydrogen.

The key issue for the implementation of pressure tanks for compressed hydrogen is strongly linked with the application of carbon fibers. This is mainly driven by the requirements of the strength of the structure and the subsequent prevention of burst cases. Following this philosophy a 750 bar tank has to have a design using high tenacity (HT) carbon fibers, which will be an issue of cost and availability. The carbon fiber market worldwide is saturated, carbon fiber raw material costs will exceed 20–25 Euro/kg, worldwide availability of carbon fibers is around 50,000 tons per annum. These boundary conditions will restrict the must-production usage of CFRP for hydrogen tanks for conventional cars.

The solution of this problem is the key to a new generation of hydrogen tank systems, whereas new promising materials for high strength fibers or filaments are currently being investigated. The most promising approach is the usage of basalt-fibers and/or super-light-weight PA-fibers such as Innegra. Table 1.1 indicates new material families for the usage of filament winding processes for



Figure 1.9 Tank assembly of the Formula H racing car, developed by the University of Applied Sciences Ingolstadt and RMIT Melbourne, see [6].



Figure 1.10 Formula H racing car at a glance.

pressure tanks. In the European project StorHy the pathway to a new generation of pressure tanks was given, also considering its current limitations to costs and availability as well as for all aspects of safety, see [5].

The usage of conventional 200 bar tanks, which may carry 1 kg of hydrogen, can be very cost efficient when used for small cars or racing projects, such as HyRacer, Formula H, and so on (Figures 1.9 and 1.10). These applications offer a wide range of easy-to-use hydrogen tank systems with ICE and conventional mechanical pressure-regulators and -reducers.

