UNIVERSITÀ DEGLI STUDI DI TRIESTE
Dipartimento di Ingegneria e Architettura

HYDROGEN STORAGE

– PART 2 –

COMPRESSED HYDROGEN

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A.A. 2023-2024

OUTLINE

1. Hydrogen Storage as a Compressed Gas
2. Hydrogen Storage as a Cryo-Compressed Gas

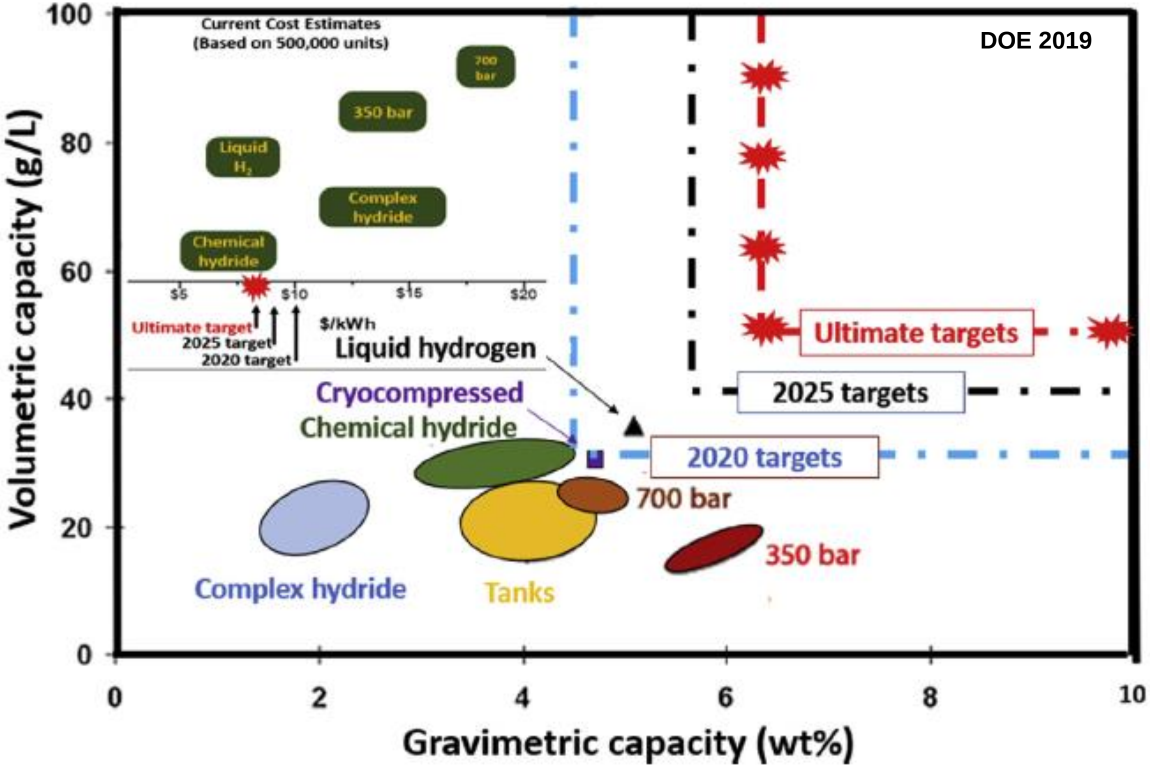
OUTLINE

Reference	Paragraph/Pages
Hydrogen production by electrolysis, Agata Godula-Jopek, 2015 Wiley	Ch. 7

Insights	
R2	Barthelemy H., Hydrogen storage: Recent improvements and industrial perspectives, Internatioanal Journal of Hydrogen Energy, 37, (2012), 17364 – 17372; DOI: http://dx.doi.org/10.1016/j.ijhydene.2012.04.121
R3	Barthelemy H. et al., Hydrogen storage: Recent improvements and industrial perspectives, Internatioanal Journal of Hydrogen Energy, 42, (2017), 7254 – 7262; DOI: http://dx.doi.org/10.1016/j.ijhydene.2016.03.178
R7	Natchane, M. et al., An Overview of the Recent Advances in Composite Materials and Artificial Intelligence for Hydrogen Storage Vessels Design J. Compos. Sci. 2023, 7, 119 ; DOI: https://doi.org/10.3390/jcs7030119

1. HYDROGEN STORAGE AS A COMPRESSED GAS

OVERVIEW



E. Boateng, A. Chen / Materials Today Advances 6 (2020) 100022

GAS COMPRESSION: INTRODUCTION NOTES

When referring to compressed hydrogen it must be taken into account that, due to the operative conditions the ideal gas law ($PV = nRT$) does not hold anymore, thus it needs to be replaced with the so-called Van der Waals equation of state:

$$\left(P + a\frac{n^2}{V^2}\right)(V - n\,b) = nRT$$

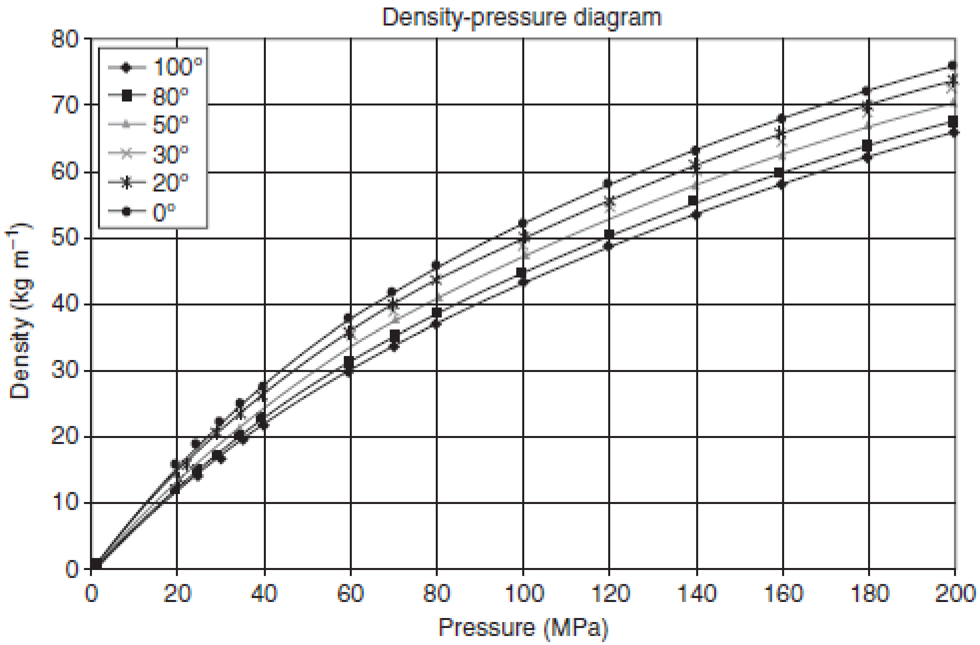
Where: *a* (equal to 24.7 10^{-6} m^6 kPa mol^{-2}) is a constant accounting for the molecular interaction (attraction/repulsion), and *b* (0.027 10^{-3} m^3 mol^{-1}) is the volume of space occupied by an hydrogen molecule.

GAS COMPRESSION: INTRODUCTION NOTES

By observing the dependence of the density profile on pressure, it is clear as hydrogen density does not increase in a linear way with increasing temperature.

At 30 MPa hydrogen density is 20 kg m^{-3} and is equal to 40 kg m^{-3} at 70 MPa.

Thus, compressing of hydrogen from the atmospheric pressure to and above 30 MPa or higher needs a large amount of energy.



GAS COMPRESSION: INTRODUCTION NOTES

Gas compression can be obtained by means of adiabatic or isothermal compression.

Adiabatic compression. There is no heat exchange takes with the environment. The amount of work required to bring the gas from the initial pressure P_1 to the final pressure P_2 can be quantified as:

$$W = \frac{\gamma}{\gamma - 1} RT_0 \left\{ \left(\frac{P_2}{P_1} \right)^{\frac{\gamma}{\gamma-1}} - 1 \right\}$$

Where γ is the specific heat ratio of the gas $(\gamma = C_P / C_V)$.

Isothermal compression. The process takes place at a constant temperature, and:

$$W = nRT \ln \frac{P_1}{P_2}$$

HYDROGEN STORAGE AS A COMPRESSED GAS

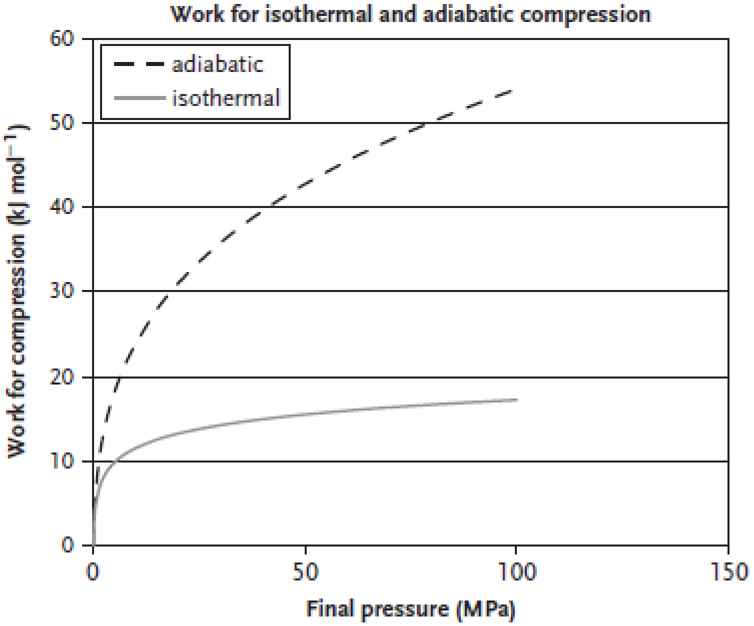
1 kg hydrogen

P_1 = 2 MPa

P_2 = 3.5 MPa

$W_{adiabatic}$ = 5.45 MJ kg^{-1}.

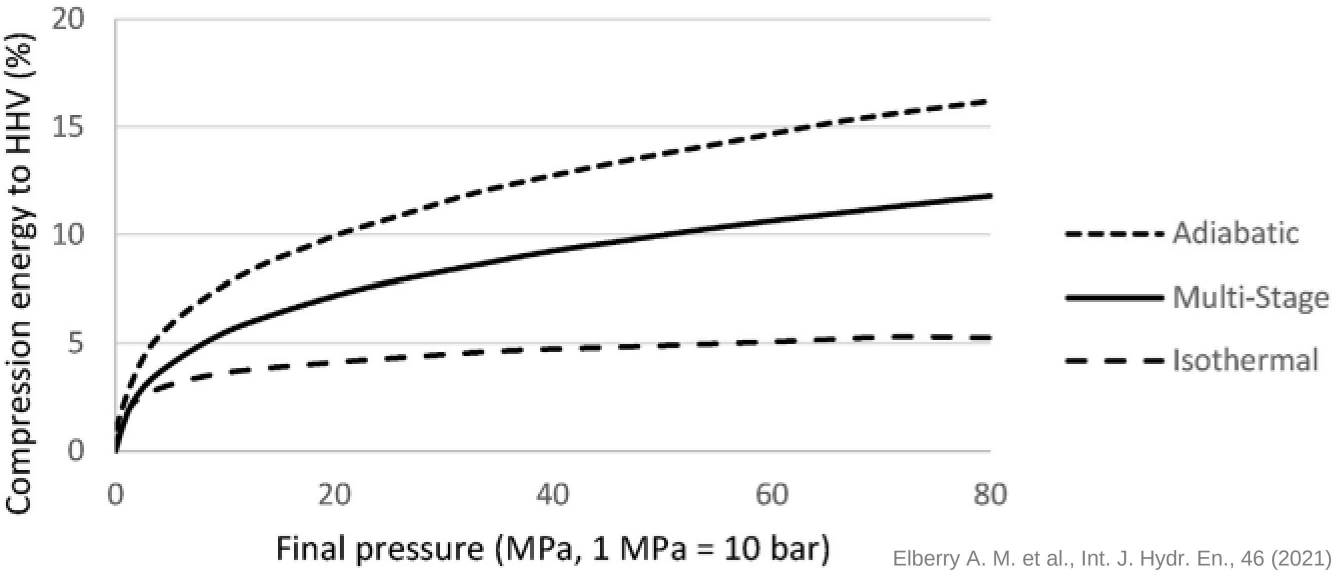
$W_{isothermal}$ = 3.03 MJ kg^{-1}.



Hydrogen Storage Technologies 4 Storage of Pure Hydrogen in Different States

HYDROGEN STORAGE AS A COMPRESSED GAS

In reality a multistage process I carried out: the gas is cooled down at firs to make the process more isothermal than adiabatic



Elberry A. M. et al., Int. J. Hydr. En., 46 (2021) 15671-15690

VESSELS FOR COMPRESSED HYDROGEN STORAGE

To date, four types of pressure vessels have been designed, characterized by cylindrical, polymorph or toroidal shape.

They are mainly made by:

- metallic parts: aluminium 6061 or 7060, steel (inox or Chrome Molybdene)
- polymer parts: polyethylene or polyamide based polymers
- composite: glass, aramid or carbon fibre embedded in epoxy resin. The fibre characteristics. Carbon fibres are preferred for 35 MPa and more applications. In the same way, various resins can be used (polyester, epoxy, phenol, etc). Epoxy resins are preferred based on their good mechanical properties, stability and compatibility with filament winding process.

VESSELS FOR COMPRESSED HYDROGEN STORAGE

R.2, R.3

To date, four types of pressure vessels have been designed, characterized by cylindrical, polymorph or toroidal shape.

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Type I tanks

- Composed by metallic walls confining the stored gas.
- This is the preferred solution for industrial applications, where hydrogen is stored at a pressure ranging from 20 to 30 MPa.
- Characterized by a low efficiency (about 1 wt% of hydrogen stored)

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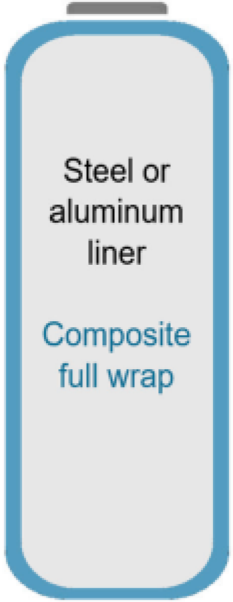
Type II tanks

- composed by a metallic linen wrapped into a fiber-resin composite.
- Employed in stationary applications where the pressure range to be used for storing is higher than 30 MPa.
- The wrapping layer is added to reduce metal liner thickness, reduce weight, and increase efficiency.

VESSELS FOR COMPRESSED HYDROGEN STORAGE



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Type III tanks

- Composed by a metallic linen fully wrapped into a fiber-resin composite. The metallic liner (usually Al) mainly acts as hydrogen permeation barrier.
- They are consistently lighter than type I and II vessels, thus more suitable for mobile applications, such in automotive.
- They are more expensive and they can withstand safely operative pressures ranging from 45 MPa to about 100 MPa.

VESSELS FOR COMPRESSED HYDROGEN STORAGE

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Type IV tanks

- Composed by a polymeric liner fully wrapped into a carbon/glass fibre composite into an epoxy matrix.
- Able to withstand up to 100 MPa.
- Expensive, still under development.

VESSELS FOR COMPRESSED HYDROGEN STORAGE

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Type V tanks

- Composed a thermoplastic liner and composite structure closely linked; the composite and the liner will be made from the same thermoplastic polymer.
- Thought to operate around 100 MPa.
- Still at the design stage, further development is required to ensure they are safe in service.

VESSELS FOR COMPRESSED HYDROGEN STORAGE

R.2, R.3

Table 1 – Key characteristics of compressed gas storage pressure vessels.

	Technology maturity	Cost performance	Weight performance
Type I	Pressure limited to 50 MPa, ++	++	–
Type II	Pressure not limited, +	+	0
Type III	For P ≤ 45 MPa (difficulty to pass pressure cycling requirements for 70 MPa, [4])	–	+
Type IV	For P ≤ 100 MPa– First commercial series – liner behaviour in gas to be further studied	–	++

Hydrogen Storage Tank Type	Energy Density (MJ/kg)	Operating Pressure (bar)	Temperature Range (°C)	Cost ($/kg H2)	Refill Time (min)
Type I	4–5	250–700	−40 to 65	$7–10	5–10
Type II	4–5	700–875	−40 to 65	$5–8	3–5
Type III	4–5	875–1100	−40 to 65	$4–6	2–3
Type IV	4–5	700–875	−40 to 65	$7–10	3–5
Type V	5–8	875–1100	−40 to 65	$5–7	2–3

Note: These values are approximate and can vary depending on various factors such as the specific design, manufacturing process, and materials used in the hydrogen storage tank. Additionally, different sources may report slightly different values.

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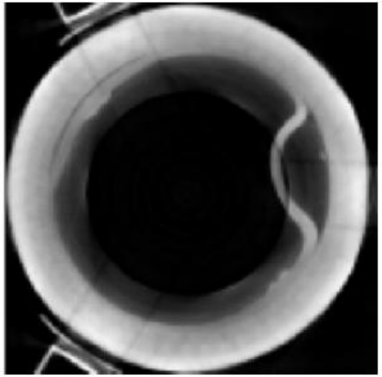
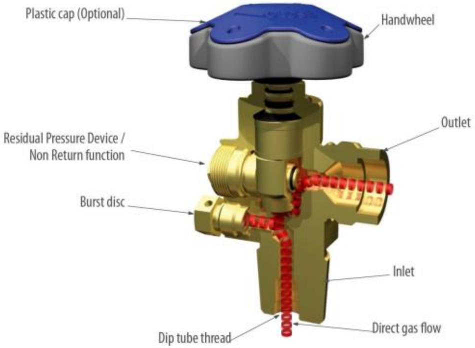
VESSELS FOR HYDROGEN STORAGE – IMPROVEMENTS REQUIRED

R.2, R.3

Hydrogen tank development still has to completely solve such issues:

- Improve material compatibility, as different materials age differently and are differently subjected to hydrogen permeation and embrittlement
- Investigate charge/discharge cycles for metallic-free tanks, as it was observed as the polymeric liner is subjected to deformations when the pressure is too much quickly released. In this extent, the installation of release pressure valves should be considered.



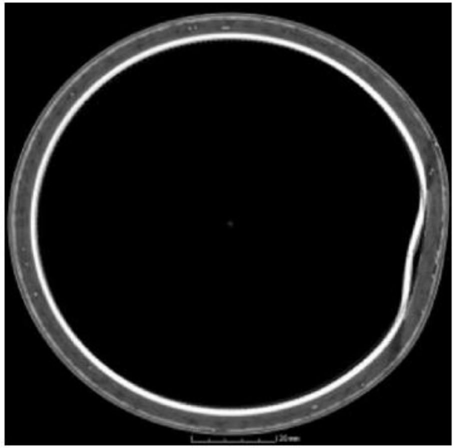


https://rotarex.com/product/rpv-valves

VESSELS FOR HYDROGEN STORAGE – IMPROVEMENTS REQUIRED

R.2, R.3

- Test the effects of accidental impacts which might occur under operation, as in example: pressure loads, environmental impact, and accidental mechanical impacts. In fact, accidental impacts might induce fiber breaking, delamination and matrix cracking of composite parts.



2. HYDROGEN STORAGE AS A CRYO-COMPRESSED GAS

HYDROGEN STORAGE AS A CRYO-COMPRESSED GAS

By storing hydrogen as a liquid, its high volumetric density is achieved and, at its boiling point (-253°C) has a volumetric density equal to 70 kg m^{-3}, extremely better than 24 kg m^{-3} of compressed hydrogen at 35 MPa (or 40 kg m^{-3} at 70 MPa).

The main drawback of liquid hydrogen is related to its energy-intensive process of liquefaction (about 25% to the 40% of the energy stored in a liquid hydrogen tank – for compression: around 10%). Moreover, vacuum-insulated vessels are needed and boil-off losses (up to 0.4%/day) cannot be avoided.

Cryo-compressed hydrogen storage was developed to alleviates these issues and combine the advantages of compassion and liquification: hydrogen is pressurized to 25 ÷ 35 MPa at cryogenic temperatures (≈ 30 K). Tanks are thus filled with a two-phase system composed by coexisting liquid and gaseous hydrogen and a volumetric density which can reach up to 87 kg m^{-3}.

HYDROGEN STORAGE AS A CRYO-COMPRESSED GAS

Cryo-compressed hydrogen appears to be the most promising solution for the automotive and road transport sectors. In 2011 BMW proposed a prototypal tank for automotive applications. The tank has a similar design to vessels used for liquid hydrogen: a type III tank is covered with a multilayered radiation shield to minimize heat transfer into the inner vessel, guaranteeing lightness and compliance to the safety requirements

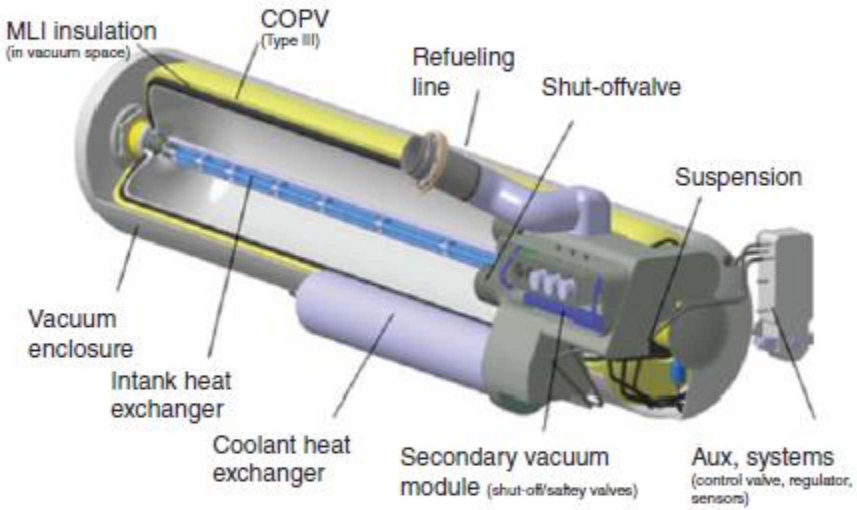


Figure 7.7 BMW prototype 2011 system layout of superinsulated cryogenic cylinder [31]. (Reprinted by kind permission of BMW.)

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