UNIVERSITÀ DEGLI STUDI DI TRIESTE

Dipartimento di Ingegneria e Architettura



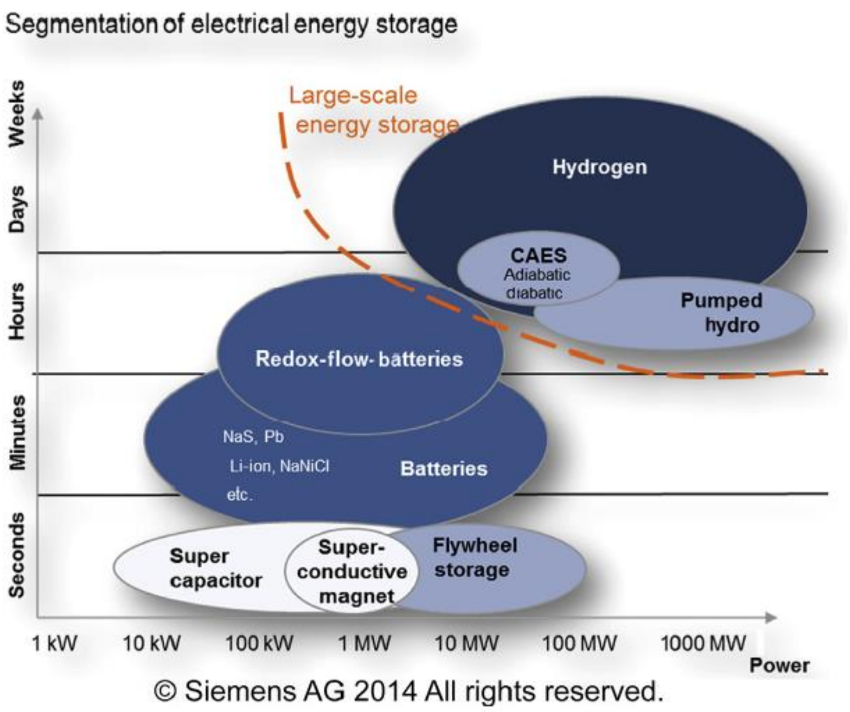


METHODS FOR HYDROGEN STORAGE

Prof. Marco Bogar

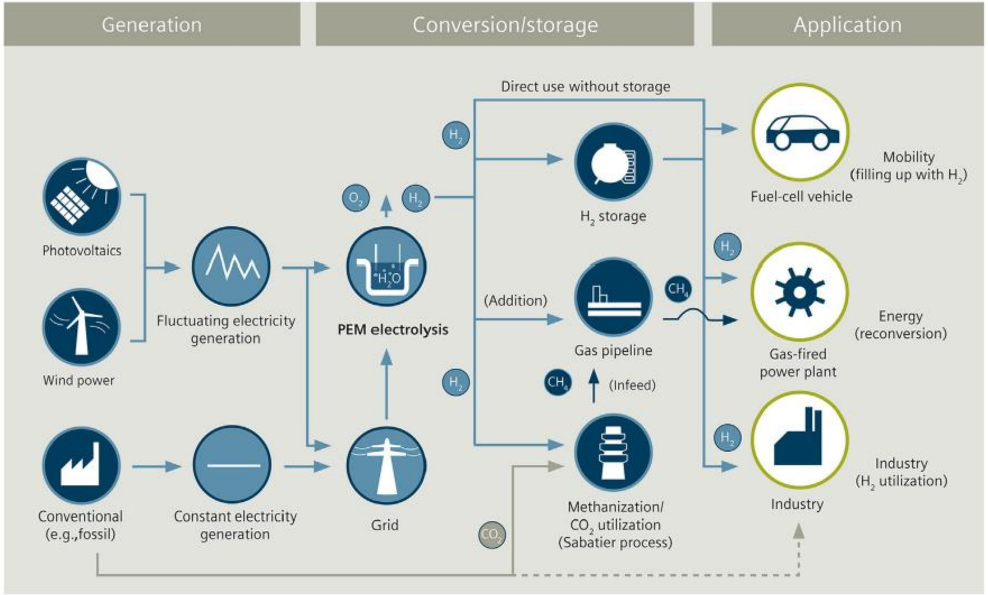
A.A. 2024-2025

HYDROGEN



Hydrogen is an energy vector, suitable for covering wide energy storage requirements. It constitutes a stable power supply and it offers a broad power range: it represents a valid alternative to batteries at a device-level (kW) and is the main choice for large-scale storage systems (GW)

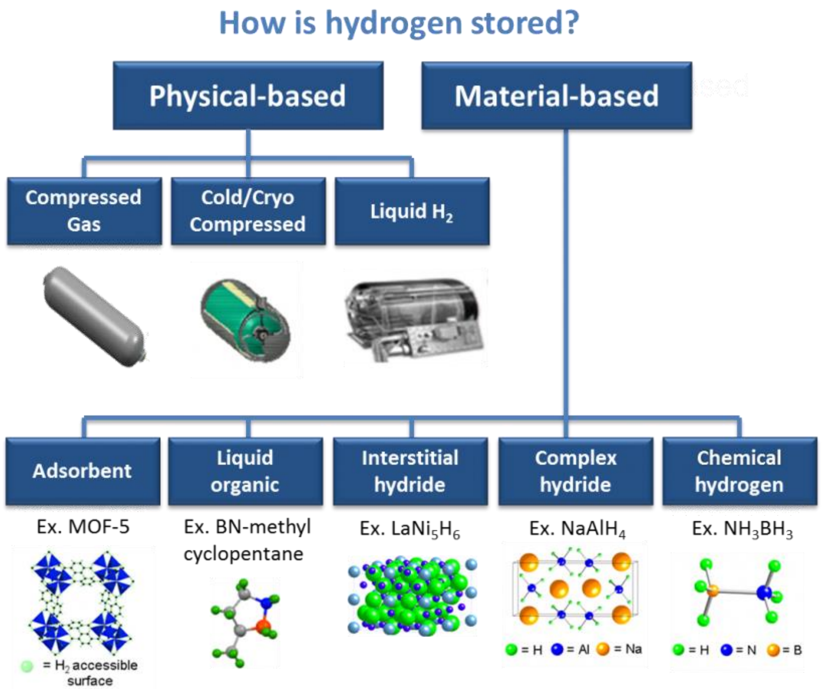
HYDROGEN PRODUCTION



Hydrogen production techniques generate gaseous hydrogen. Depending on the application, hydrogen needs to be:

- Directly used
- Streamed into a pipeline
- Stored

STORAGE METHODS CLASSIFICATION



Storage methods classification

Physical-based methods:

- Compressed in high-pressure gas tanks
- Cold/cryo compressed
- Liquified in cryogenic tanks

Material-based methods:

- Physisorption
  - Hydrogen is adsorbed on materials with a large specific surface area
  - Hydrogen is absorbed on interstitial sites in a host metal
- Chemisorption
  - Hydrogen is chemically bonded in covalent and ionic compounds (at ambient pressure)
  - Hydrogen oxidation of reactive metals

STORAGE METHODS / OBSERVATIONS FOR MOBILE APPLICATIONS

Storage method	Energy intensity (MJ/kg-H_2)	wt%-H_2/tank	wt%-H_2/kg-system	g-H_2/tank	g-H_2/L-system
Compressed H_2 (35 MPa)	10.2	6	4–5	20	15
Liquid H_2	28–45	20	15	63	52
Low-temperature hydrides ($T < 100°C$)	10–12	2	1.8	105	70
High-temperature hydrides ($T > 300°C$)	20–25	7	5.5	90	55

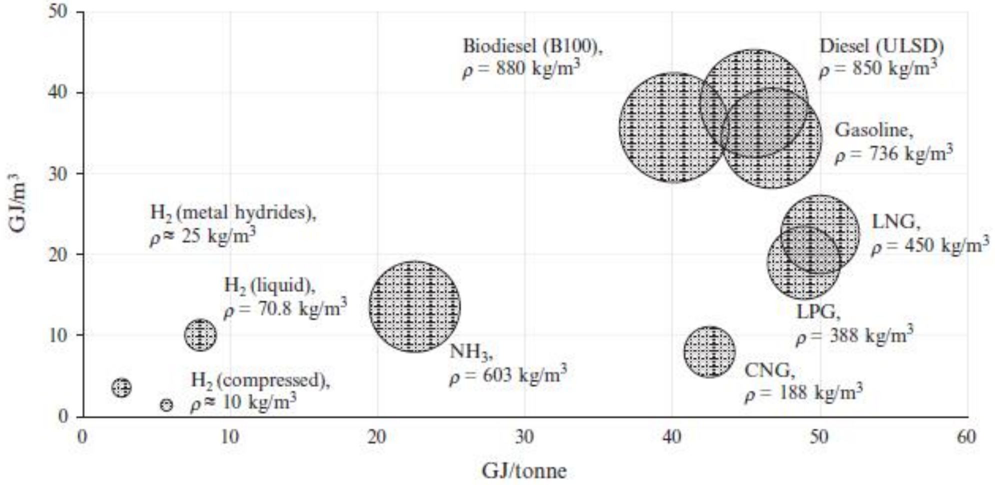


FIG. 2.22 Volumetric (GJ/m^3) and gravimetric (GJ/tonne) energy density and mass storage density (kg/m^3) of transportation fuels.

STORAGE METHODS / OBSERVATIONS FOR MOBILE APPLICATIONS

For stationary applications gravimetric and volumetric densities are not so critical due to available space and weight. There is also possible to operate at higher pressures and temperatures.

On contrary, for mobile applications several improvements still need to be adopted; in particular:

- Being able to operate at low pressures and at temperatures in the range of −50 to 150 °C because of safety concerns and for reducing management costs
- Improve process kinetics of hydrogen loading and recharging
- Contain costs of hydrogen storage
- Reach higher volumetric (Wh/L) and gravimetric (Wh/kg) energy densities to limit storage occupancy and weight on portable devices.

COMPARISON OF HYDROGEN STORAGE METHODS

Physical storage methods

1. Compressed hydrogen
2. Liquid hydrogen
3. Cooled/cryogenic hydrogen

Material-based storage methods (solid hydrogen storage)

4. Hydrogen physisorption
5. Hydrogen chemisorption

COMPRESSED HYDROGEN / THERMODYNAMICS

As with any pure substance, the thermodynamic state of hydrogen is completely defined by specifying two independent intensive state variables (temperature, pressure, specific volume).

At ambient conditions hydrogen fulfils the ideal gas law:

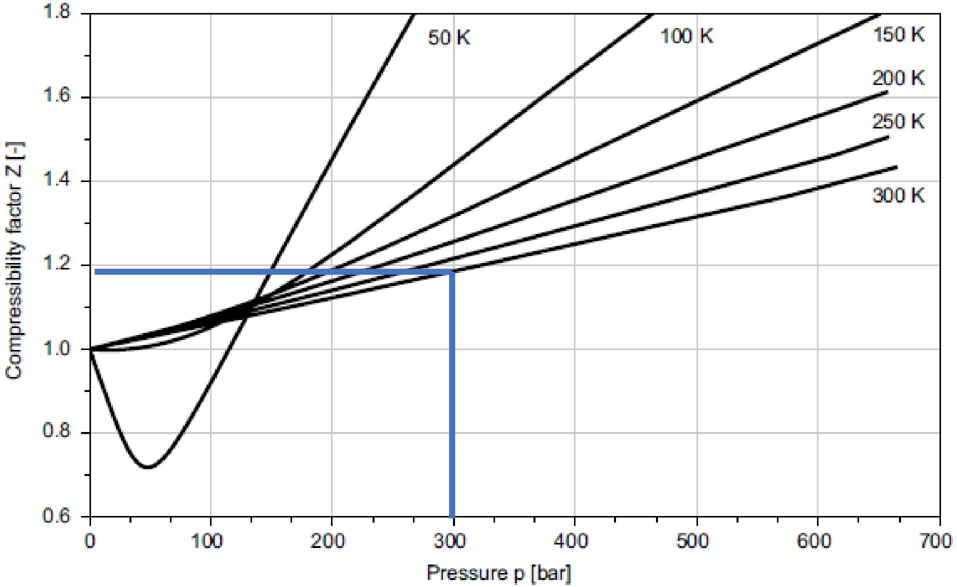
$$PV = mRT$$

Where m is the product between the number of moles and the molar mass. The ideal gas law can be improved by including the (dimensionless) compressibility factor:

$$Z = \frac{PV}{RT} = \frac{PV_m}{RT_m}$$

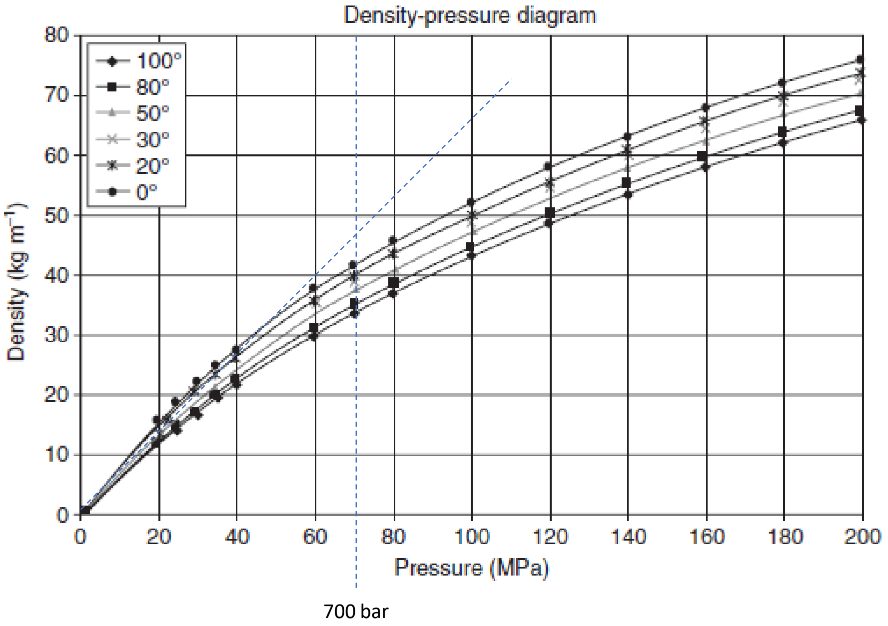
The deviation of Z from the value ‘1’ can be determined to measure the deviation of the gas from the ideal behaviour

COMPRESSED HYDROGEN / THERMODYNAMICS



At 300K and 300 bar, Z ≈ 1.2: a calculation of the hydrogen mass in a container from a measurement of temperature and pressure using the ideal gas equation will result in a mass 20% greater than in reality.

COMPRESSED HYDROGEN / HYDROGEN COMPRESSION



Hydrogen density does not increase in a linear way with increasing temperature. Thus, hydrogen compression is needs a larger energy amounts for achieving higher compression rates.

COMPRESSED HYDROGEN / HYDROGEN COMPRESSION

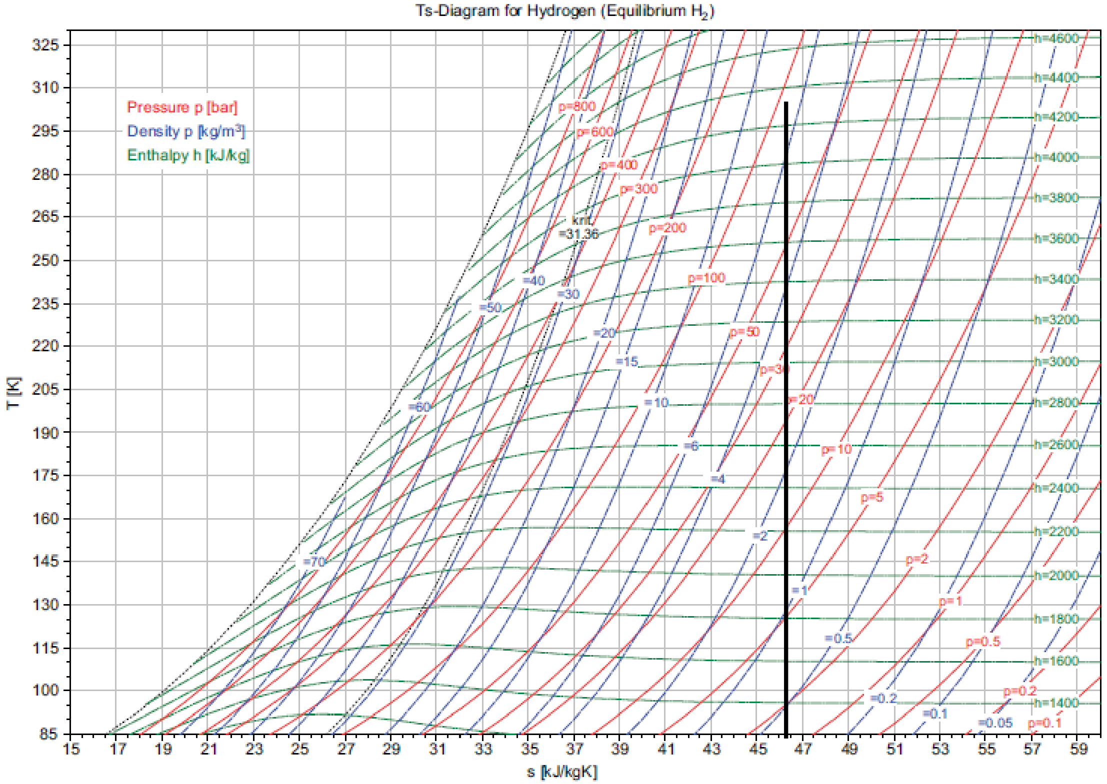
Isothermal compression

Temperature is kept constant by means of a heat exchanger; $\Delta T = 0$

Adiabatic compression

No heat is exchanged with the surroundings: $Q = 0$

COMPRESSED HYDROGEN / ISOTHERMAL COMPRESSION



For isothermal compression, heat involved in the process must be estimated at first.

It can be done by using T-S diagrams, where temperature variation is plot in function of system entropy at constant pressure, density, and enthalpy.

Heat is estimated by calculating the area underneath the selected curve

$$Q = \int T dS$$

Note. T-S diagrams can be also used to calculate specific heat capacity as:

$$c = \frac{dQ_{rev}}{dT} = T\frac{dS}{dT}$$

COMPRESSED HYDROGEN / ISOTHERMAL COMPRESSION

Moreover, for an isothermal process the work required to compress hydrogen from starting (1) to the final (2) states can be defined as:

$$W_i = \int_1^2 V dP$$

Where, for an ideal gas, V can be expressed by means of the ideal gas law and:

$$W_i = \int_1^2 \frac{RT}{P} dP$$

$$\boxed{W_i = RT \ln \frac{P_2}{P_1}}$$

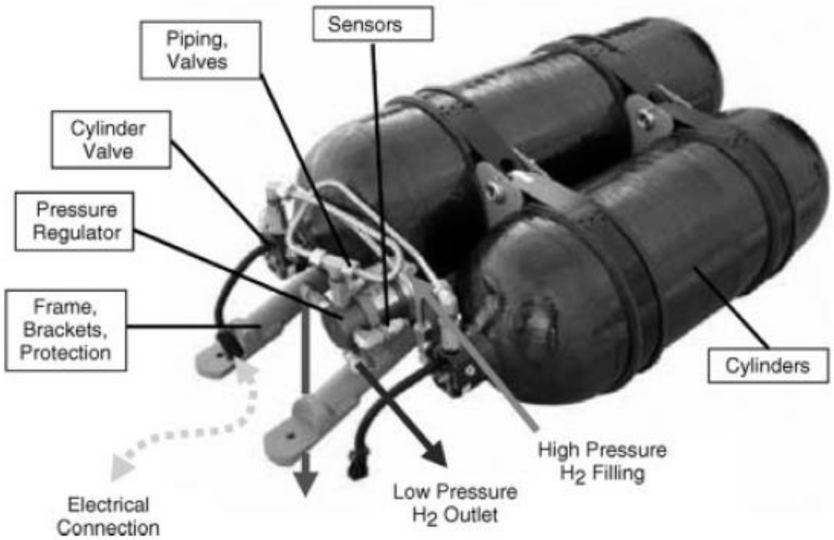
COMPRESSED HYDROGEN / ADIABATIC COMPRESSION

On contrary, in case of adiabatic compression, the work required to compress hydrogen from the starting point (1) to the final one (2) is:

$$W_a = \frac{\gamma}{\gamma - 1} RT \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma}{\gamma-1}} - 1 \right]$$

where γ is the ratio between the specific heat at constant pressure (C_P) and the specific heat at constant volume (C_V): $\gamma = C_P / C_V$

COMPRESSED HYDROGEN / STORAGE



Compressed hydrogen is the preferred option for storing and distributing hydrogen (especially for the automotive sector).

In fact, gas pressurization is a widely used and established technology; advancements can be rapidly implemented.

COMPRESSED HYDROGEN / CONTAINERS

Compressed hydrogen is provided in containers at either at 30 MPa (300 bar) or 70 MPa (700 bar).

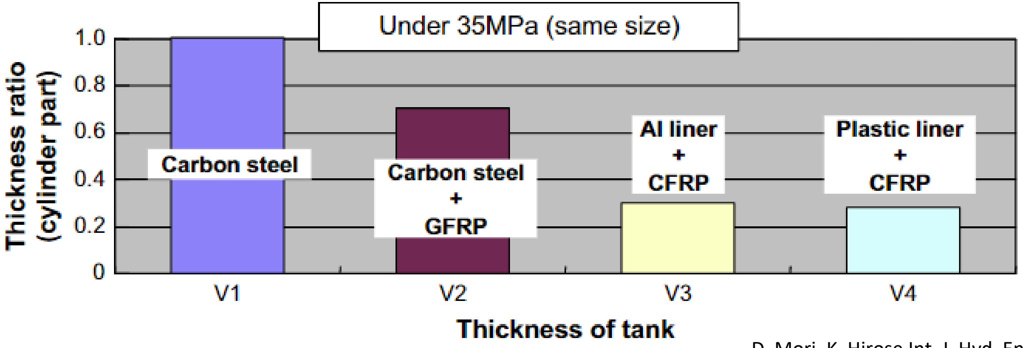
Overall in the latter case, it has been mandatory to develop proper hydrogen containers using composite materials. In fact, Hydrogen has a tendency to adsorb and dissociate at material surfaces; hydrogen then diffuses into the material and causes embrittlement and diffusion. Materials suitable for hydrogen applications are mainly austenitic stainless steel. Moreover hydrogen containers shall be designed in order to:

- Avoid hydrogen embrittlement and permeation
- Be resistant to external corrosion
- Be resistant to dynamic and impact loads
- Ba able to prevent hydrogen leaks
- Guarantee compatibility with static and cyclic pressurization.
- Resistant up to 140°C during the fast filling procedure

COMPRESSED HYDROGEN / CONTAINERS

Containers for compressed hydrogen can be classified in four types:

	V1	V2	V3	V4
composition	All Metal	Metal Liner + GFRP layer (hoop lap)	Metal Liner + CFRP layer (full lap)	Plastic Liner + CFRP layer (full lap)



D. Mori, K. Hirose Int. J. Hyd. En., 34, 10, 2009, 4569-4574

COMPRESSED HYDROGEN / CRITICAL ISSUES

- Work required for compression represents the main limitation because it increases production costs. It can be estimated as about the 20% of the specific energy content of the compressed hydrogen is used for gas compression.
- Delivery of highly-compressed gas to low-pressure system cannot be immediate in order to avoid abrupt temperature rise. Refill process has to be kept in closed control.
- Safe hydrogen management is demanding due to high gas activity (flammable and explosive in concentration 4 ÷ 74.5%).
- Low volumetric and gravimetric storage energy densities, compared to gasoline.

Property	200-Bar Vessel	400-Bar Vessel	700-Bar Vessel
Internal volume (L)	50	50	50
Vessel diameter (m)	0.3	0.3	0.3
Vessel length (m)	1.0	1.0	1.0
Vessel weight (kg)	25	45	85
Stored energy (kWh)	24	43	66
Stored H_2 (kg)	0.7	1.3	2.0
Vessel-to-hydrogen weight ratio	35.7	34.7	42.5
Weight specific energy storage (kWh/kg)	0.96	0.96	0.78
Volume specific storage (kWh/L)	0.48	0.86	1.32

1 tank of gasoline (52 kg) has the same heat of combustion of 10kg of hydrogen

COMPARISON OF HYDROGEN STORAGE METHODS

Physical storage methods

1. Compressed hydrogen
2. Liquid hydrogen
3. Cooled/cryogenic hydrogen

Material-based storage methods (solid hydrogen storage)

4. Hydrogen physisorption
5. Hydrogen chemisorption

LIQUID HYDROGEN

Liquid Hydrogen
It is produced by compressing, cooling and expanding hydrogen.

Critical temperature:	33.25 K	−239.9 °C	
Fully liquid:	20 K	−253.15 °C	ambient pressure
	33.25 K	−239.9 °C	13 bar

It has been extensively used in industrial processes since the 1940s thus the technology for managing it is well established. It can be achieved by means of:

- the Precooled Linde-Hampson process
- the Claude process
- the helium hydrogen cycle.

LIQUID HYDROGEN / PRODUCTION – THE CLAUDE PROCESS

In a first stage, liquid nitrogen is used to cool hydrogen down to 80 K

Then a two-stage Brayton cycle cryogenic refrigerator is used to produce liquid hydrogen

A two-phase liquid / vapour hydrogen is introduced in a tank

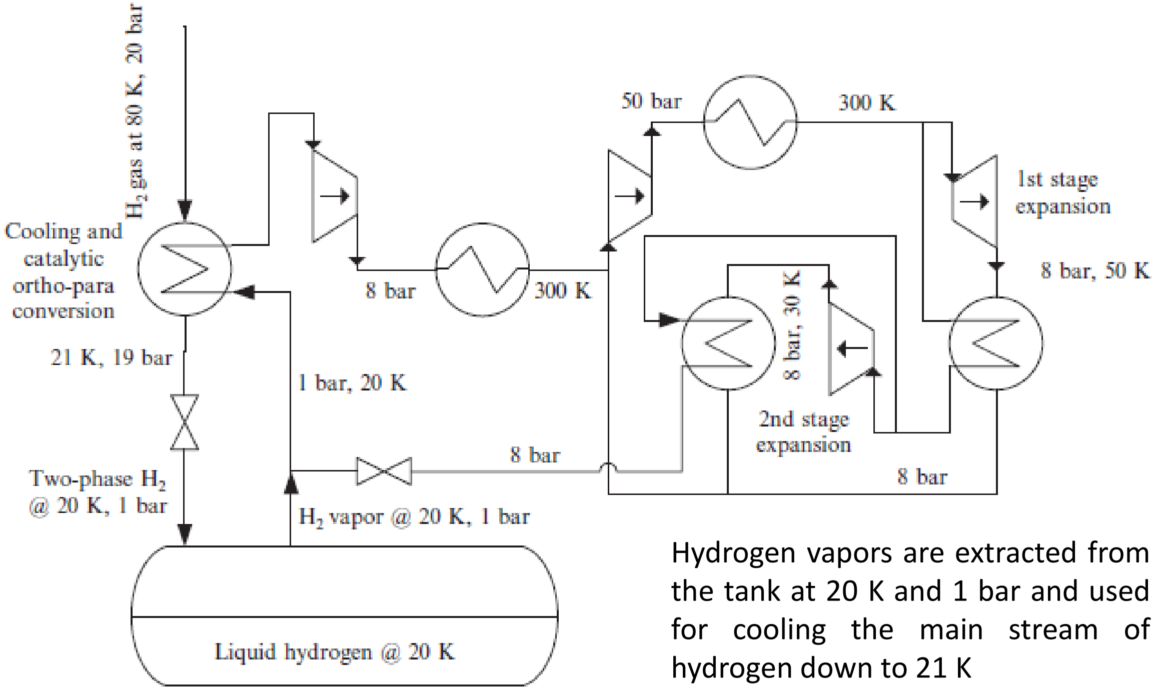
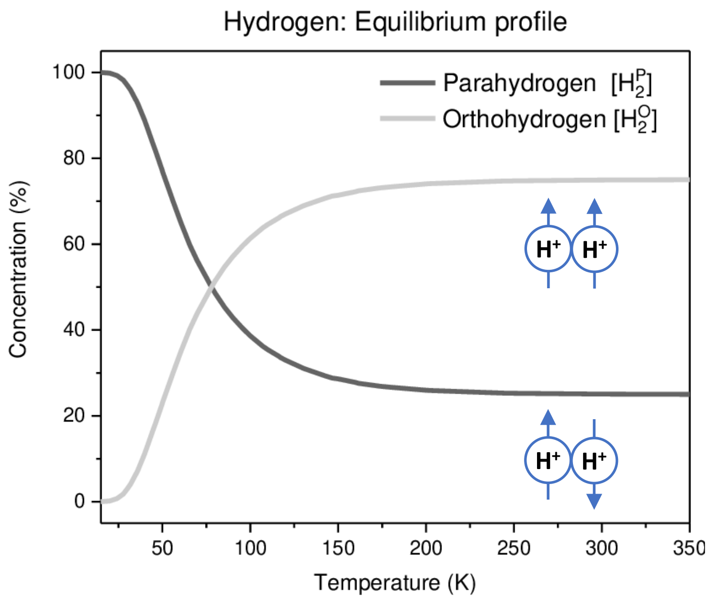


FIG. 2.23 Simplified diagram of Claude hydrogen liquefaction process.

Hydrogen vapors are extracted from the tank at 20 K and 1 bar and used for cooling the main stream of hydrogen down to 21 K

HYDROGEN CONDENSATION / BOIL OFF (1)



Karlsson, E. (2017). Catalytic ortho- to parahydrogen conversion in liquid hydrogen.

During hydrogen condensation process, the conversion from ortho-hydrogen to para-hydrogen taxes place.

This conversion is exothermic, and the ratio of H_2^O/H_2^P is temperature dependent.

In example, at 77 K the enthalpy of conversion is equal to 523 kJ/kg.

Enthalpy of conversion becomes a source of heat which cannot be avoided and induces hydrogen evaporation which has to be vent in the environment to reduce system pressure.

HYDROGEN CONDENSATION / BOIL OFF (2)

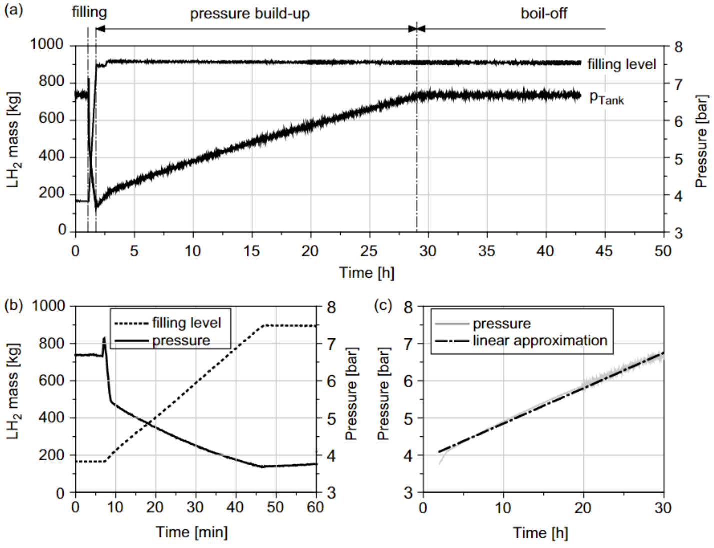


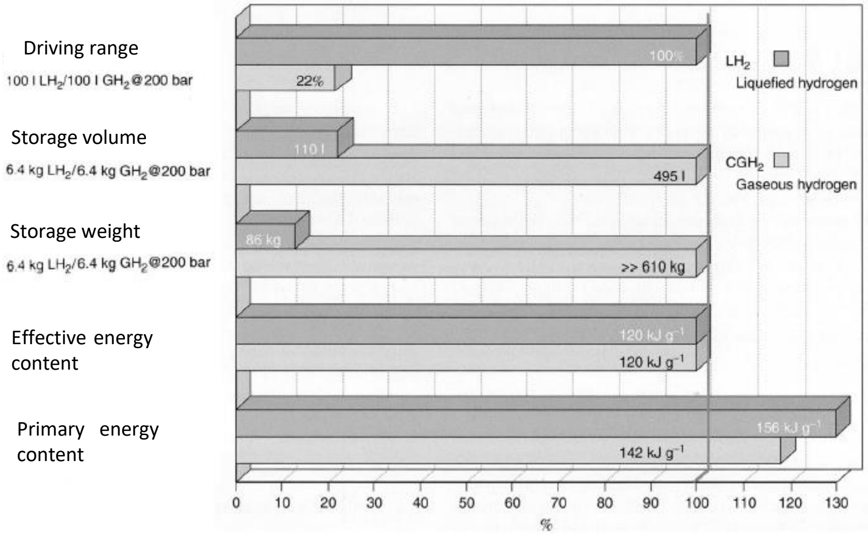
Figure 1.9 (a) Measurement of pressure and filling level in the tank versus time and in more detail: (b) during filling process, (c) during pressure build-up.

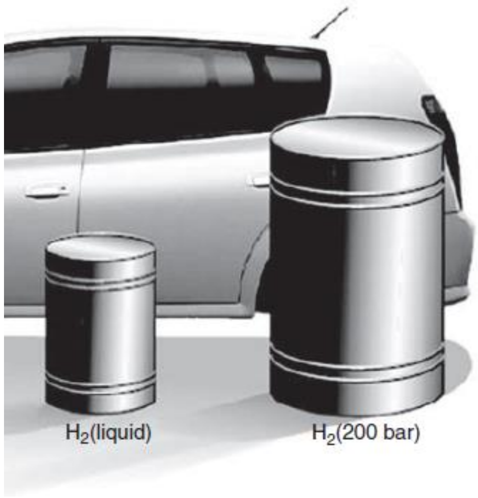
Handbook of Hydrogen Storage: New Materials for Future Energy Storage

- Filling. The pressure in the tank is reduced to enable liquid hydrogen to flow into the container from the trailer along a pressure gradient.
- Pressure build-up. Due to the unavoidable heat input, hydrogen evaporates in the tank (unwanted loss). Thus the pressure rises in the vessel. Pressure rise can be regarded as being linear over time.
- Boil-off. From reaching maximum system pressure of 6.7 bar in our case, the tank is an open system and hydrogen is blown out. From then, the pressure remains constant, the filling level decreases constantly. The vaporization rate and/or the rate of the effusing hydrogen is about 0.5 kg H_2 per hour

LIQUID HYDROGEN / MAIN ADVANTAGES

Main advantages are related to high volumetric and gravimetric energy density, low pressure operation, and it allows quick refill process





LIQUID HYDROGEN / CRITICAL ISSUES

- Boil-off constitute a process loss which cannot be avoided
- The energy loss required to prepare the liquid fuel is up to the 30% of the total specific energy content.
- Overall for automotive, the storing and distribution system has to be optimized.
- Cryogenic management has to guarantee safety requirements.

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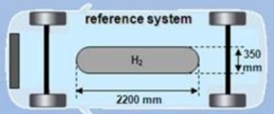
CRYO-COMPRESSED HYDROGEN

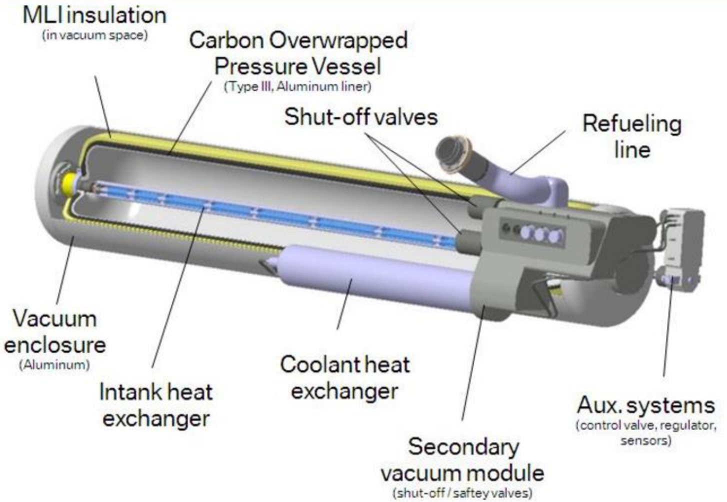
- Hydrogen is stored at cryogenic temperatures (≈ 30 K) in a pressurized container in between 250 and 350 bar (25 ÷ 35 MPa).
- The stored fluid can be composed by cold compressed hydrogen or by a mixture of hydrogen in a two-phase region (saturated liquid and vapour)
- This technique represents a compromise between liquid hydrogen and compressed gas storage at ambient temperatures.

COMPRESSED HYDROGEN TECHNOLOGY / CONTAINERS

Super-insulated cryogenic COPV (Type III) 35 MPa (CcH_2)	
Max. usable capacity	CcH_2: 8 kg (265 kWh) CGH_2: 2.7 kg (90 kWh)
Operating pressure	2 – 35 MPa
Vent pressure	35 MPa
System weight (inluding H_2)	~145 kg
Refueling pressure	CcH_2: 30 MPa CGH_2: 35 MPa
Refueling time (20% – 100%)	< 4 min
Mean dormancy time	CcH_2: > 10 days CGH_2: years
H_2-Loss Leakage: Infrequent driver:	<< 3 g/day < 2 % / year



- + Active tank pressure control
- + Load carrying vehicle body integration
- + Engine/fuel cell waste heat recovery
- + Compatible with 350bar CGH_2 refueling



Thus operational envelope covers pressures of up to 35 MPa (350 bar) and temperatures from 338.15 K (+65 °C) down to 33.15 K (−240 °C).

CRYO-COMPRESSION TANK / OUTLOOK

- Compared with the hydrogen storage tanks available today, the cryo-compressed storage tanks have the highest system-based volumetric and gravimetric energy storage densities.

- It has a low (5 to 16 times) adiabatic expansion energy which increases the safety of this technology in case of refilling failures

- Refilling station need only to be provided with a cryo-pump and a liquid hydrogen storage tank; there is no need for high-pressure tank arrays and additional equipment such as heat exchangers and gas compressors.

- On contrary, heat transfer with the environment has to be limited and production is still energy expensive.

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SOLID HYDROGEN STORAGE / OUTLOOK

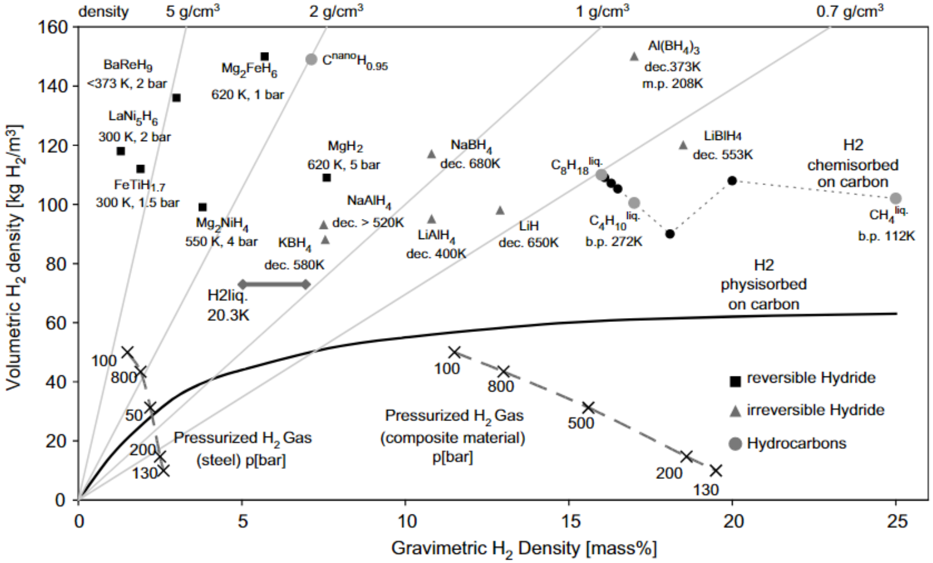


Figure 1.25 Density of hydrogen storage technologies.

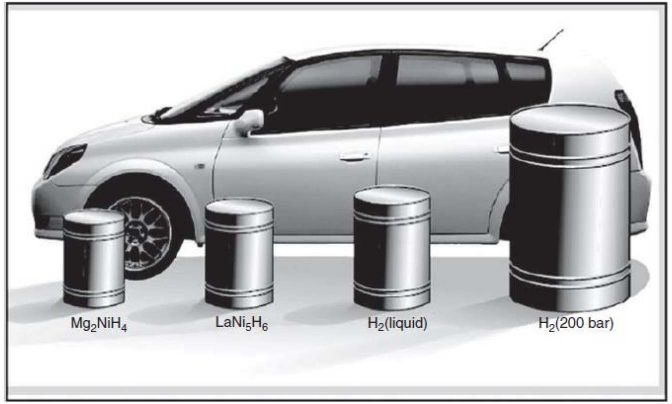


Figure 7.9 Alternatives for storage of 4 kg hydrogen with volume relative to the size of a car [32].

Regarding volumetric storage density, storage of hydrogen in compounds has the greater potential: more hydrogen per unit can be stored in compounds than in the pure form.

SOLID HYDROGEN STORAGE / OUTLOOK

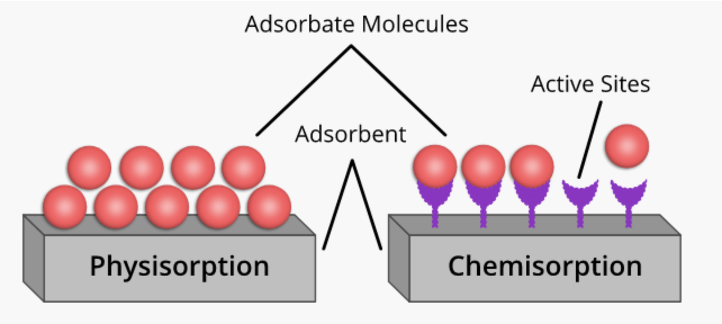
Main advantages:

- Theoretically presents better energy efficiency with respect compressed and liquified hydrogen
- They allow to operate in more safety conditions
- Most of the problems related to the use of high pressures and low temperatures (*e.g.* boil off, …) are not present

Main disadvantage:

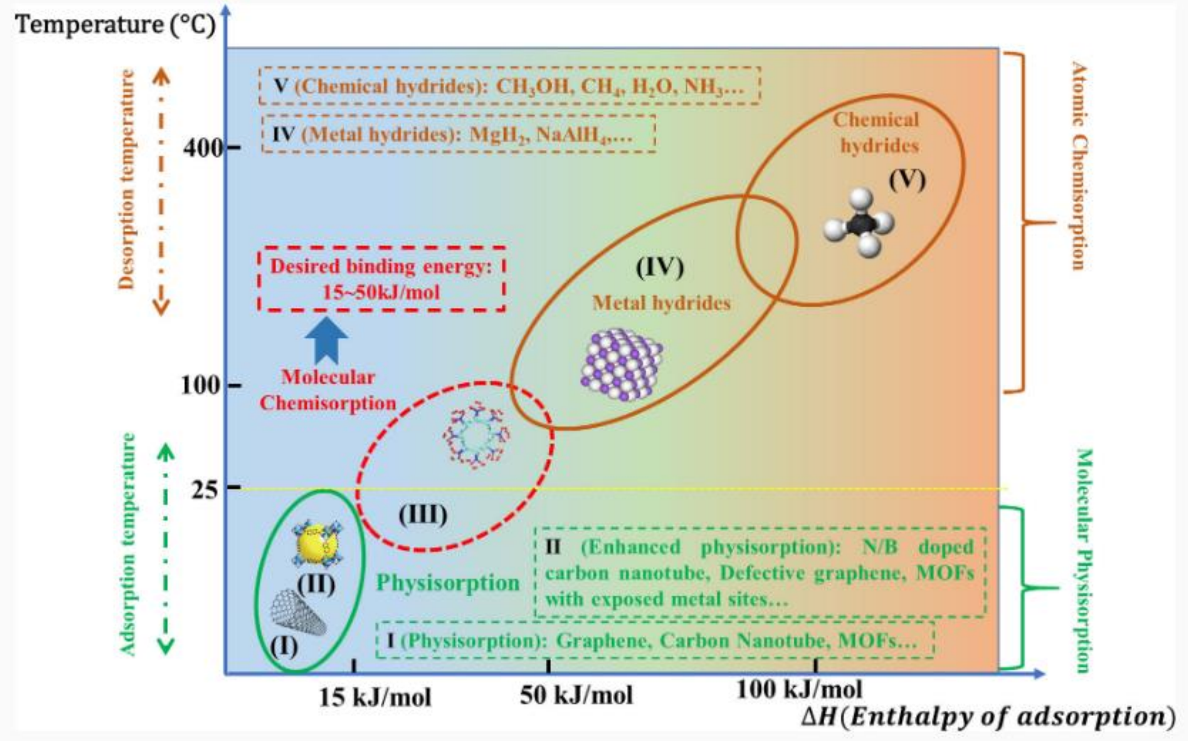
- An efficient and compact way of storing hydrogen in a solid state for mobile applications has not been clearly identified yet. The lack of a suitable hydrogen storage material currently limits the utilization of hydrogen more widely in the automotive sector, especially in fuel cell vehicles.

SOLID HYDROGEN STORAGE / PHYSISORPTION AND CHEMISORPTION



Physisorption	Chemisorption
H_2 is adsorbed at the surface by Van der Waals interactions	H_2 is chemically held into reaction sites by chemical bonds
In order to get adsorbed, the hydrogen molecule needs to be displaced in close contact with the surface (around one molecular radius)	Storing and release requires bond formation or breaking energy
It takes place below 0°C (273 K) and/or at high pressures	It takes place at high temperatures
Completely reversible; no activation energy is needed	Activation energy is required
Hydrogen can be stored in multilayers	Monolayer phenomenon

SOLID HYDROGEN STORAGE / PHYSISORPTION AND CHEMISORPTION

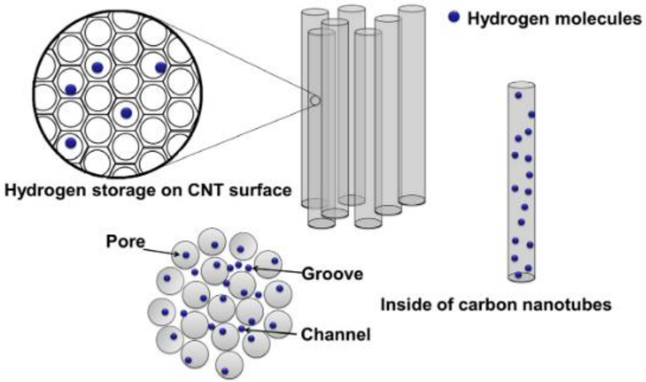


Lang et al., *Chem Synth* 2022;2:1.10.20517/cs.2021.15

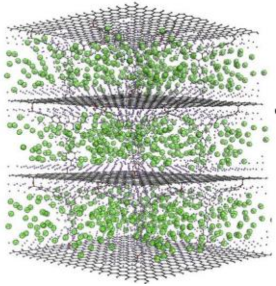
SOLID HYDROGEN STORAGE / PHYSISORPTION

Preferential materials are constituted by materials with a high specific surface area. Among them, carbon-based nanoporous materials such as:

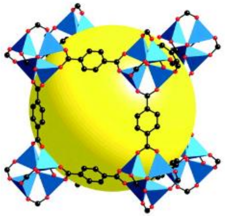
- single-walled carbon nanotubes (SWNTs)
- multi-walled carbon nanotubes (MWNTs)
- Graphite
- Graphene layered structure
- Metal-Organic Frameworks (MOFs)



R.S. Rajaura et al. / Nano-Structures & Nano-Objects 14 (2018) 57–65



Öztürk Z., Int. J. Hydrogen Energy 46, 21, (2021), 11804-11814



Rosi et al.,Science 300, 5622 (2003), 1127-1129

SOLID HYDROGEN STORAGE / CHEMISORPTION

Preferential materials for hydrogen chemisorption are selected in function of their thermodynamic properties and their kinetics of dehydrogenation.

According to the type of materials which are used, chemisorption can be further divided into:

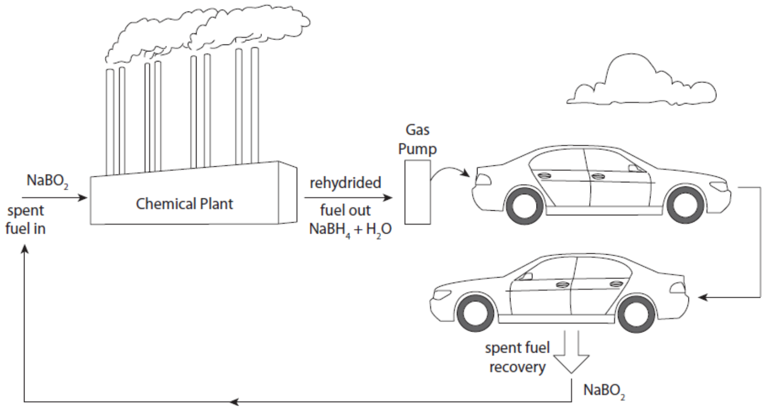
- Chemical hydride storage
- Metal hydride storage

SOLID HYDROGEN STORAGE / CHEMICAL HYDRIDE STORAGE

Hydrogen is stored in materials which are made react with water; hydrogen release reaction is exothermic, as an example:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 + heat$$

Other chemical hydrides are CaH_2, $LiAlH_4$ or MgH_2; also organic compounds can be used.



- Rapid and controlled hydrogen generation, storage and transportation
- High hydrogen storage density
- The spent fuel can be recycled and recharged

- Hydride regeneration reaction is expensive
- Additional steps and complexity are added at the supply chain with respect compressed hydrogen

SOLID HYDROGEN STORAGE / METAL HYDRIDE STORAGE

In metal hydride storage, bonding of hydrogen to a metal is controlled by means of thermodynamic conditions (set of temperature and pressure).

Hydrogen storage and release can be thus finely controlled at the desired rates in reversible reactions:

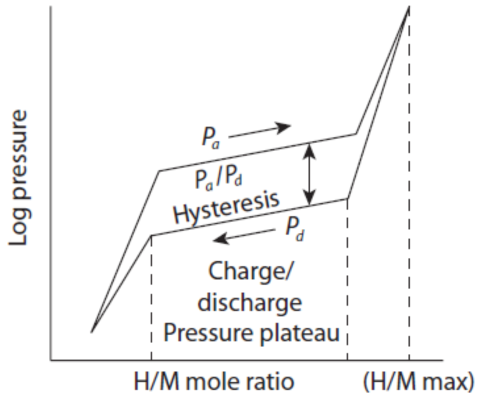
$$Me + \frac{x}{2} H_2 \leftrightarrow MeH_x$$

In addition to metals also intermetallic compounds and alloys can be used.

Solid hydride are finally composed by solid particles with high surface area.

CHEMISORPTION / METAL HYDRIDE STORAGE

To compare different materials, isothermal charging and discharging cycle diagrams are used, where pressure (0.3 – 3 MPa is a common application range) is plot with respect hydrogen storage fraction (amount of hydride per mole; maximum values around 2). The hysteresis between adsorption and desorption pressures is due to different process kinetics



- The most elemental metal hydrates does not show satisfying performances
- Intermetallic compounds properly designed by mixing a strongly hydriding and a poorly hydriding element have formulated to enhance storage capacity

SOLID HYDROGEN STORAGE / SYSTEM EXAMPLE

Electrolyser coupled Solid-State Hydrogen Storage System

The world's first unit, coupling industrial-scale electrolyser with 100 kg solid state hydrogen storage unit (energy content of 3.3MWh), based of magnesium hydride MgH_2 (6.7wt%) as a hydrogen source was developed in Grenoble in 2013.

- totally reversible hydrogen storage
- high cycling stability
- energy, costs and maintenance savings when compared to existing hydrogen storage solutions
- significant reduction in safety risk when compared
- to compressed or cryogenic storage

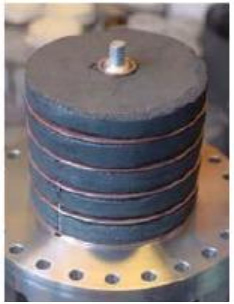
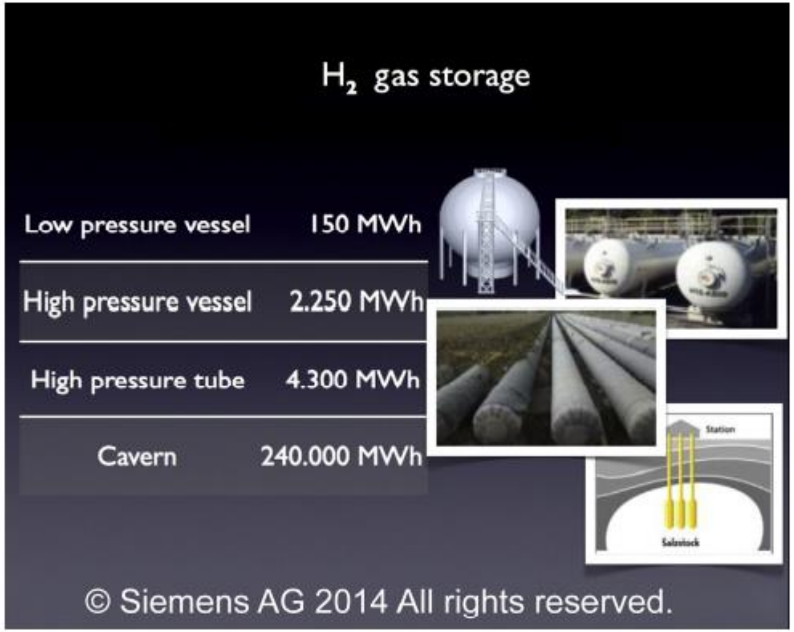
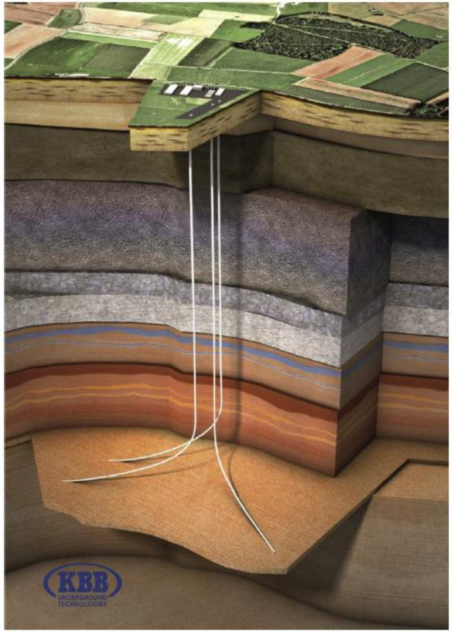


Figure 7.20 McLyzer 60, McPhy aggregates hydrogen production skid units to create larger-output hydrogen production units of 60 $Nm^3 h^{-1}$ at 12 bar) allowing optimization of costs and energy efficiency. (Reprinted by kind permission of McPhy Energy, Grenoble, France.)

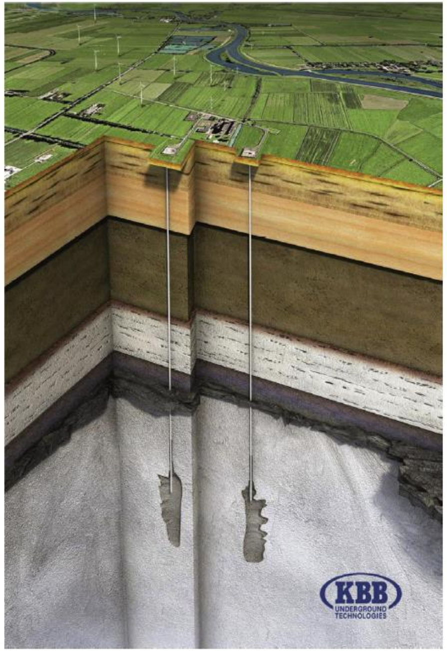
LARGE SCALE HYDROGEN STORAGE METHODS



UNDERGOUND HYDROGEN STORAGE



Gas storage in depleted oil and gas fields.



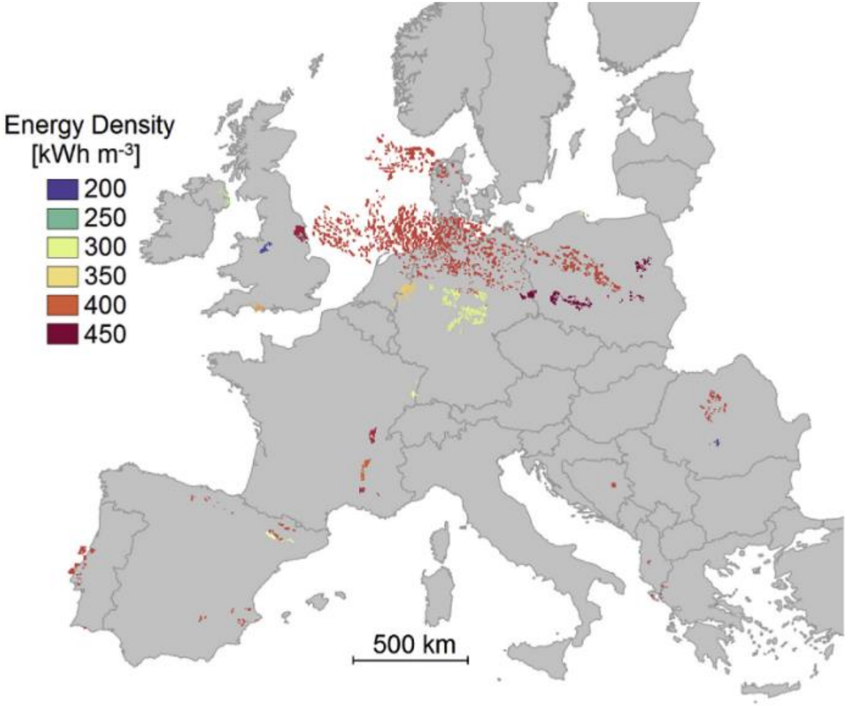
Artificial underground salt cavern.

UNDERGOUND HYDROGEN STORAGE

Salt formations at depths of several 100 meters offer a series of suitable and beneficial conditions for the construction and operation of high-pressure gas storages:

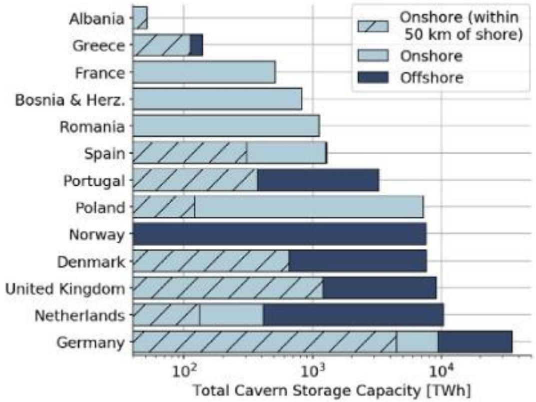
- Extremely high gas tightness of rock salt even at high pressure
- High operational pressures at depths of down to almost 2000 m allowing high energy densities due to the higher operation pressure of the cavern
- Geometrical volumes of 500,000 m^3 and above allowing storage capacities of several thousand tons hydrogen
- Small land footprint on the surface
- Low specific investment costs per megawatt-hour of storage
- Very secure against manipulation and obstruction
- High-pressure NG is also stored in depleted oil fields, and preferably gas fields aquifer formations, saline groundwater-bearing porous reservoir

UNDERGOUND HYDROGEN STORAGE



Caglayan D. G. et al., International Journal of Hydrogen Energy, 45, 11, 2020, 6793-6805

Total on- and offshore European hydrogen storage potential estimated at 84.8 PWhH_2.
Onshore salt caverns within 50 km of the coast constitute 7.3 PWhH_2 (~30%).
Highest national storage potential is observed in Germany with 9.4 PWhH_2.



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