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PAE

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Hydrogen Storage New Technologies

Introduction

- Hydrogen storage is a key enabling technology for the advancement of hydrogen and fuel cell technologies in applications including stationary power, portable power, and transportation.

- As an energy storage medium, the essence of fuel cell is to convert between chemical energy and electrical energy through the oxidation of hydrogen. However, although the specific energy of hydrogen is large (142 MJ/kg, the highest of any practical fuel), its volumetric energy density is very low: only 12.1 MJ/m3 at 288.15 K and 1 atm.

- As a bridge between hydrogen production and utilization, one of the key points of hydrogen storage technology is to increase the energy density of hydrogen. Yet other factors must be taken into consideration when evaluating the pros and cons of hydrogen storage technology, such as safety, transportation cost, difficulty of hydrogenation/dehydrogenation, etc.

Source: Courtesy of integralnewenergy.com

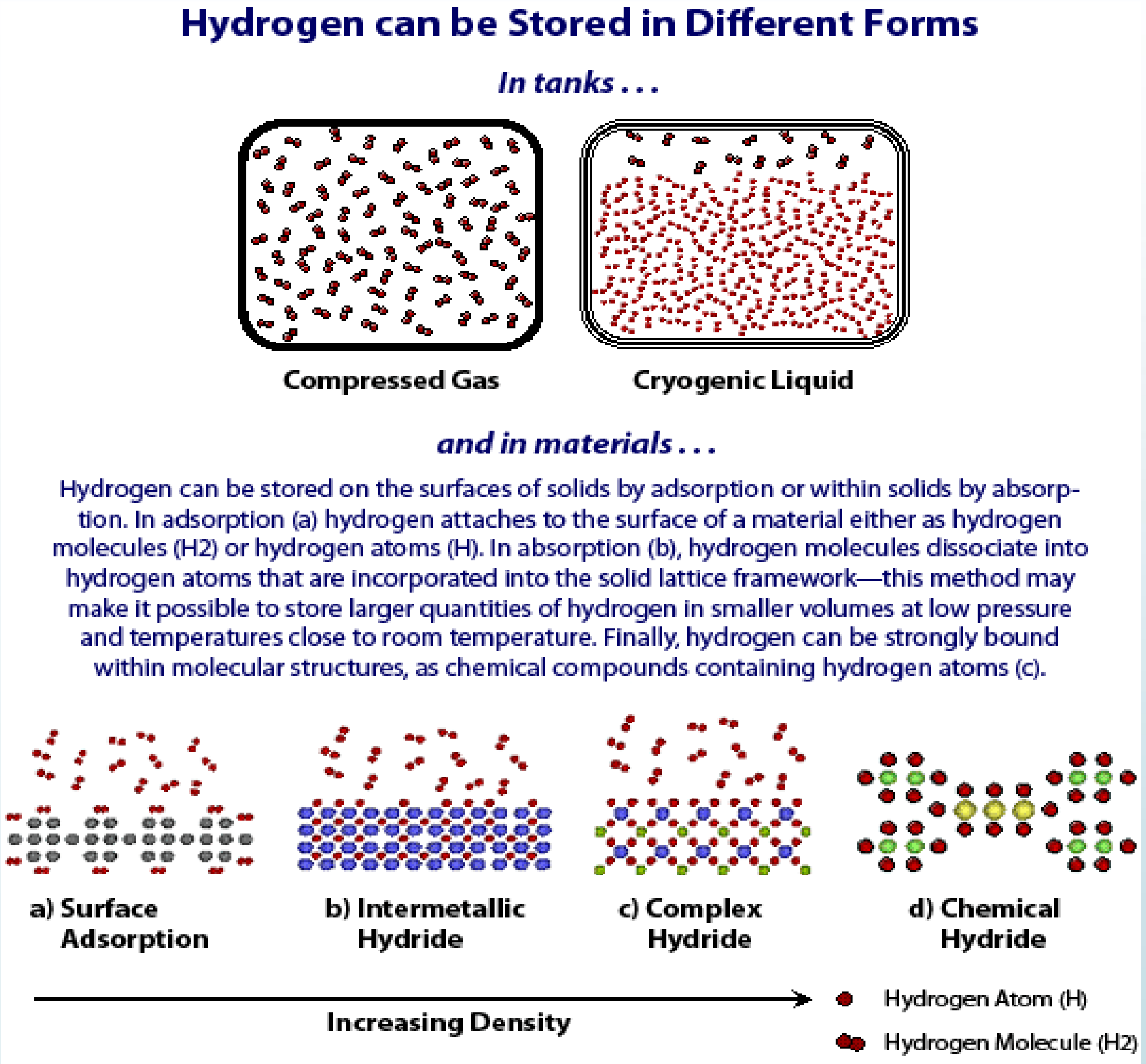
How Hydrogen Storage Works

Hydrogen storage technologies mainly include physical, chemical hydrogen storage technologies.

Physical hydrogen storage technology refers to a technology that store hydrogen simply by changing the physical storage conditions to increase the hydrogen density. This does not require a hydrogen storage medium, has lower cost, and the dehydrogenation process is relatively easy. **High-pressure gaseous hydrogen** and **cryogenic hydrogen** storage are two most typical physical hydrogen storage technologies in China (Figure 1).

Chemical hydrogen storage technology is a technology that uses storage carrier to react with hydrogen under certain conditions to generate stable compounds (hydrogenation), and then changes the conditions to achieve hydrogen release (dehydrogenation). Current carriers include liquid organic hydrogen carrier (LOHC), metal hydride, liquid ammonia, etc.

Source: Courtesy of integralnewenergy.com



Hydrogen can be Stored in Different Forms

In tanks . . .

and in materials . . .

Hydrogen can be stored on the surfaces of solids by adsorption or within solids by absorption. In adsorption (a) hydrogen attaches to the surface of a material either as hydrogen molecules (H2) or hydrogen atoms (H). In absorption (b), hydrogen molecules dissociate into hydrogen atoms that are incorporated into the solid lattice framework—this method may make it possible to store larger quantities of hydrogen in smaller volumes at low pressure and temperatures close to room temperature. Finally, hydrogen can be strongly bound within molecular structures, as chemical compounds containing hydrogen atoms (c).

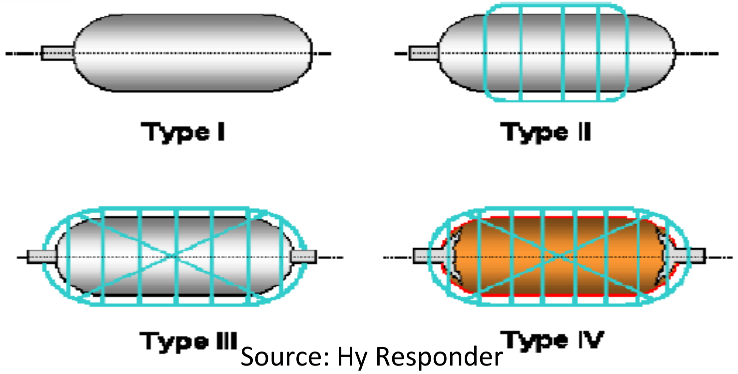
Figure 1 Comparison of different hydrogen storage technologies
Reference: Energy.gov

Hydrogen Storage Technologies

1. Gaseous Hydrogen

By compressing with high pressure, hydrogen is compressed and charged into a hydrogen storage vessel. This hydrogen storage method is now the most commonly used and mature technology. The materials for manufacturing hydrogen vessels have also gone through various generations and have formed different standards.

Type I—all-metal cylinders
Type II—all-metal cylinders with hoop-wrapped composite
Type III—fully wrapped composite cylinders with metallic liners
Type IV—fully wrapped composite cylinders with non load bearing nonmetallic liners



Source: Hy Responder

All-metal vessels (often steel) are commonly used for high-pressure gas compression storage with operating pressure as high as 700 bars. However, for hydrogen storage, steel is not a desirable material. It is because the diffusion of hydrogen into steel causes hydrogen embrittlement failure, especially when the vessels undergo frequent charge and discharge. In the case of rupture, steel fragments may cause serious injuries. Steel vessels are heavy and have low gravimetric storage density. Such problems can be resolved by using vessels made of composite materials comprised of polyethylene, or carbon fiber and epoxy resin with thin aluminum liner and by ameliorating the material wrapping methods.
These different type of vessels have different properties and thus would be used in different cases of hydrogen application scenarios such as, **transportation**, **stationary** hydrogen storage and **onboard** hydrogen storage.

Source: Courtesy of integralnewenergy.com

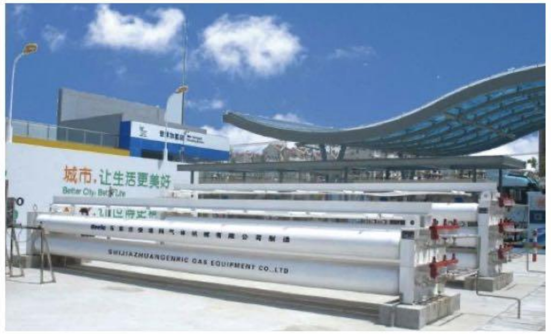
Hydrogen Storage Technologies > Gaseous Hydrogen > (Stationary Hydrogen Storage and Transportation Storage)

(1) For **Stationary Hydrogen Storage** and **Transportation Storage**

- Two storage pressures are available according to downstream onboard storage pressure demand: 45MPa (supply to 35MPa tank) and 98MPa (supply to 70MPa tank).
- Instead of purchasing all high-pressure storage tanks, hydrogen station can minimize required compression pressures, compression time, and overall system cost by using cascade storage system: low (20-30 MPa), medium(30-40 MPa), and high (40+ MPa).
- Sometimes the hydrogen storage tube trailer is also used as in-station storage facility.

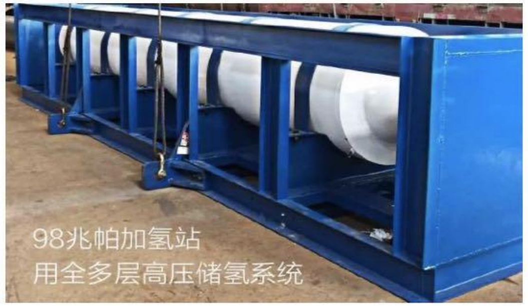
Source: Courtesy of integralnewenergy.com

Hydrogen Storage Technologies > Gaseous Hydrogen > (Stationary Hydrogen Storage and Transportation Storage)

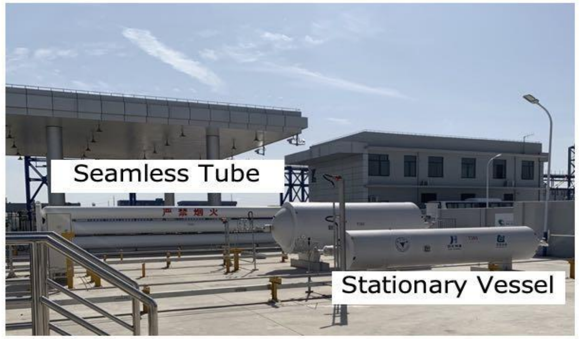


45MPa stationary storage vessel in Lijiang HRS, CIMC Enric

45MPa stationary storage vessel delivered in Zhejiang, REIN



98MPa stationary storage vessel in Changshu HRS, Zhejiang University & Juhua



Jinshan HRS, equipped with storage tube and stationary storage vessel

Figure 2: Two main types of high-pressure hydrogen storage containers in Hydrogen Refueling Stations in China
Reference: Public information, Summarized by Integral

- **Seamless tube (Type I storage vessel)** : Most widely adapted storage vessel in HRS in China. Usually have 20MPa (both for transportation and stationary use, more common) and 45MPa (only for stationary use).
- **Stationary flat steel ribbon wound vessel:** Domestically initiated technology in China. China has completely independent intellectual property rights in the design and manufacturing of this storage vessel. There usually have 45MPa (capacity can reach 20 m3) and 98MPa (capacity can reach 1 m3).
- **Type III storage vessel**: there are also 45MPa and 98MPa type. Compared with 20MPa seamless tube, higher storage pressure require less space and can bear more hydrogen. Yet due to technical constraints, only few companies are manufacturing type III storage vessels. More R&D work is still needed before it can be widely applied in China. Higher storage capacity in HRS is required as the local hydrogen demand increase, however, type III tank may replace type I tank which is the most commonly adapted in Chinese HRS.

Hydrogen Storage Technologies > Gaseous Hydrogen > (Onboard Hydrogen Storage)

(2) For **Onboard Hydrogen Storage**

- Type I and II cylinders are impractical for automotive applications where weight and volume play a critical role in defining the overall efficiency of the vehicle. As such, most recent efforts at developing high-pressure, compressed cylinders for light-duty vehicles has been devoted to **Type III and IV cylinders**.

- For both types, there are two working pressure: 35 MPa and 70MPa. Although it is more widely used internationally is type IV cylinder, **type III cylinder still enjoys its market dominancy in China, especially for 35MPa tank** (70MPa type III are currently under final process of testing validation, see Figure 3)

Source: Courtesy of integralnewenergy.com

Hydrogen Storage Technologies > Gaseous Hydrogen > (Onboard Hydrogen Storage)

35MPa Type III tank: Realize domestic production in scale and have been widely applied in FCEV

Storage Tank Manufacturer	Application
Shenyang Gas Cylinder Safety Technology (CLD) 沈阳斯林达	• 2010 Shanghai World EXPO FCEV Pilot Program • SAIC FC Tour Bus in 2010 Guangzhou Asian Games • Dongfeng Special Automobile • SUNWIN
Beijing Chinatank Industry 北京科泰克	• Foshan Public Transport • Young Man Bus • MAXUS FCV80
Furuise 富瑞氢能	• Dongfeng Special Automobile
Tianhai Industry 天海工业	• XXIV Olympic Winter Games Vehicle

70MPa Type III tank: Most players in active development and test stage for possible application in FCEV.

Status	Storage Tank Manufacturer	Note
Test Validation	Shenyang Gas Cylinder Safety Technology 沈阳斯林达	• Applied in Roewe 950 FCV since 2016 • Already signed contract with SAIC Motor, GAC Group、SinoHytec 亿华通, etc. • Successfully passed critical step:氢循环试验
	Beijing Chinatank Industry 北京科泰克	
Tank onboarding	Furuise 富瑞氢能	
Sample Delivery to Whole-vehicle manufacturer	Tianhai Industry 天海工业	
	中材科技	• Undergo certification process for 70MPa tank

Figure 3. Market player of type III storage tank in China

Reference: Public information, summarized by Integral

Hydrogen Storage Technologies > Gaseous Hydrogen > (Onboard Hydrogen Storage)

(2) For **Onboard Hydrogen Storage**

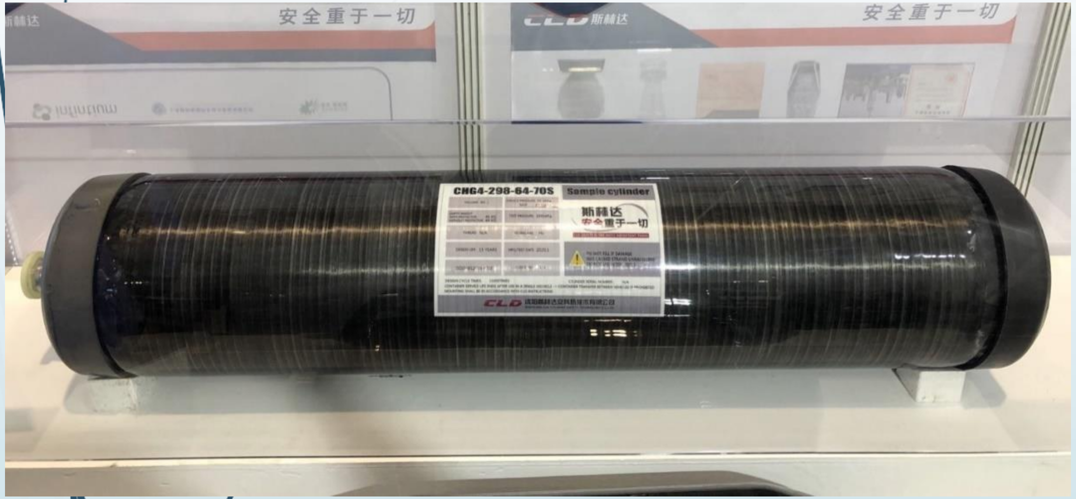


Figure 4 70MPa Type IV cylinder, exhibited by CLD
Reference: 5th FCVC Exhibition & Integral

- Since there was once an accident on type IV tank caused by the leakage of hydrogen gas and type IV tank was, therefore, forbidden to be sold in China.
- Also, other factors have confined the development of type IV tank. Heavy reliance on foreign suppliers, for instance, carbon fibers from Toray Industries, largely restricted the price and output of the tanks.
- Nevertheless, type IV storage tank still has advantages over type III tanks in many aspects. For example, it has less weight and longer lifetime. Some vessel failure could be avoided by using non-metallic materials, such as hydrogen embrittlement.
- Shenyang CLD, exhibited their uncommercialized 70MPa type IV hydrogen storage vessel at the 5th FCVC (Fuel Cell Vehicle Congress) (Figure 4).

Source: Courtesy of integralnewenergy.com

Hydrogen Storage Technologies > Cryogenic Hydrogen

2. Cryogenic Hydrogen

Compared with high-pressure gaseous hydrogen, cryogenic hydrogen storage has several advantages:

- **Higher hydrogen storage capacity and lower storage pressure**: can be adapted to larger hydrogen demand in the future as well as decrease the required hydrogen station size
- **Higher hydrogen purity**: can increase the life of fuel cells. In the liquefaction process, impurities will also be solidified, and the purity can thus be further improved.
- **Economic advantage in larger volume and long distance**

With the development in hydrogen and FCEV industry, hydrogen demand is expected to increase greatly. In addition, in face of hydrogen demand and supply imbalance in some region, the transportation of hydrogen from hydrogen-abundant region (e.g. renewable energy source provinces where excess of hydrogen will be generated) to demand region will also appear. The economies of scale will render the transportation via cryogenic hydrogen more attractive.

Source: Courtesy of integralnewenergy.com

Hydrogen Storage Technologies > Cryogenic Hydrogen

2. Cryogenic Hydrogen

In China, currently there are basically two types of civil liquid hydrogen projects:

1) those undertaken by private enterprises and mainly for station use;
2) those undertaken by SOEs, mainly for energy management (scale-up projects using curtailed RE power) (Figure 5). The latter one has much larger capacity, they can be ten or hundred times larger than previous type of project. These serves as demonstration projects, and take years to be fully commercialized.

	Project Name	Participated Enterprise	City	Project Timeline	Planned Capacity
(private)	广东省液氢试验检测基地项目	Fullcryo 中科富海 GDSEI 广东省特检院	Foshan Guangdong	2020 - 2022	0.2-0.3 ton/day
	鸿达兴业乌海液氢项目	Hongda Xingye 鸿达兴业 Wuhai Chemical Industry乌海化工 101 Institute 中国航天101	Wuhai Inner Mongolia	- 2020	0.5 ton/day
	浙能集团液氢产业项目	Zhejiang Energy Group浙江能源 101 Institute 中国航天101	Jiaxing Zhejiang	- 2020	1 ton/day
	大同100MW光伏制氢（液化）项目	Datang International Thermo Electric Company 山西大唐国际云冈热电	Datong Shanxi	2020 -	Phase I 8 ton/day Phase II 10 ton/day
	美国AP氢能源及配套产业基地项目	Air Products	Jiaxing Zhejiang	2020 -	25~40 ton/day (Phase I 13.3 ton/day)
(SOE)	中国三峡集团风电制氢液化外送项目	CTG 长江三峡集团	Ulanqab Inner Mongolia	2020 -	10 ton/day
	中石化集团洛阳炼化氢能一体化（含液氢工厂）项目	Sinopec 中国石化	Luoyang Henan	- 2023	Phase I 8 ton/day Phase II 10 ton/day
	国家电投集团湖南核电液氢产业基地项目	Sinopec 中国石化 CNNC (Hunan) 湖南核电	Yueyang Hunan	Phase I - 2023 Phase II - 2025	Phase I 20 ton/day Phase II 40 ton/day
	同煤集团山西大同液氢产业基地项目	Datong Coal Mine Group 大同煤矿集团	Datong Shanxi	Phase I - 2023	Phase I 10 ton/day Phase II 30 ton/day Phase III 100 ton/day

Figure 5 List of civil liquid hydrogen projects , Reference: Public information, summarized by Integral

Source: Courtesy of integralnewenergy.com

Hydrogen Storage Technologies > Carrier Technology: LOHC

3. Carrier Technology: LOHC

- The LOHC technology is based on the chemical bonding of hydrogen to liquid organic carriers (LOHC), which are mostly aromatic hydrocarbons or heterocyclic substances. The loading takes place via an exothermic hydrogenation reaction, the discharge via an endothermic dehydrogenation. In contrast to some other chemical hydrogen storage processes, these reactions are reversible.
- The carrier molecule is cycled between a loaded (LOHC+) and unloaded (LOHC-) state. The worldwide research and development work in the field of LOHC is based on different LOHC substances, such as dibenzyltoluene (Hydrogenious, Germany), benzene or toluene (Chiyoda, Japan) and N-Ethylcarbazole (Hynertech, China).
- Compared to other technologies, storage via LOHC has several advantages:
  - **Easy to handle:** storage under ambient temperature and pressure, which greatly reduces the cost of handling hydrogen (without great liquefaction or gas compression cost).
  - **Easy to transport**: using conventional chemicals, existing oil & chemicals infrastructure can be used for the storage and transportation.
  - **Chemically stable**: already converted to liquid chemical (loaded LOHC+), there is very minor loss by **long term storage** & long distance transport.

Source: Courtesy of integralnewenergy.com

Hydrogen Storage Technologies > Carrier Technology: LOHC

3. Carrier Technology: LOHC

Future operation of central LOHC hydrogenation plants are possible at locations where a large amount of curtailed RE-generated hydrogen is produced and **stored in long term**.

Loaded LOHC+ can be transported via standard chemical tank trucks to the hydrogen refueling stations, which are equipped with a dehydrogenation system.

There, the hydrogen can be produced when needed and then integrated into the existing hydrogen refueling station technology.

Source: Courtesy of integralnewenergy.com

Hydrogen Storage Technologies > Carrier Technology: Metallic Hydride

4. Carrier Technology: Metallic Hydride

- Metals or alloys can also be applied as carrier for the storage of hydrogen. In presence of a catalyst, hydrogen molecule is dissociated into atoms, which will then diffuse into the lattice of the metal and form metallic hydrides.
- Light metals such as Li, Be, Na, Mg, B and Al, form a large variety of metal–hydrogen compounds. One reason they are especially interesting is due to their light weight, which might increase the gravimetric storage density.
- There are considerable researches on magnesium(Mg) and its alloys for onboard hydrogen storage due to their high hydrogen-storage capacity and low cost. Besides, the Mg-based hydrides possess good-quality functional properties, such as heat-resistance, vibration absorbing, reversibility and recyclability. In recent years, therefore, much attention has been paid to investigations on specific material properties of Mg alloys for the development of new functional materials.
- The formed metal hydride leads to a solid-state hydrogen storage under moderate temperature and pressure, which gives them the important safety advantage over the gas and liquid storage methods.

Source: Courtesy of integralnewenergy.com

Hydrogen Storage Technologies > Carrier Technology: Metallic Hydride

4. Carrier Technology: Metallic Hydride

However, before the commercialization of metallic hydride as storage material, there are more things to be tackled:

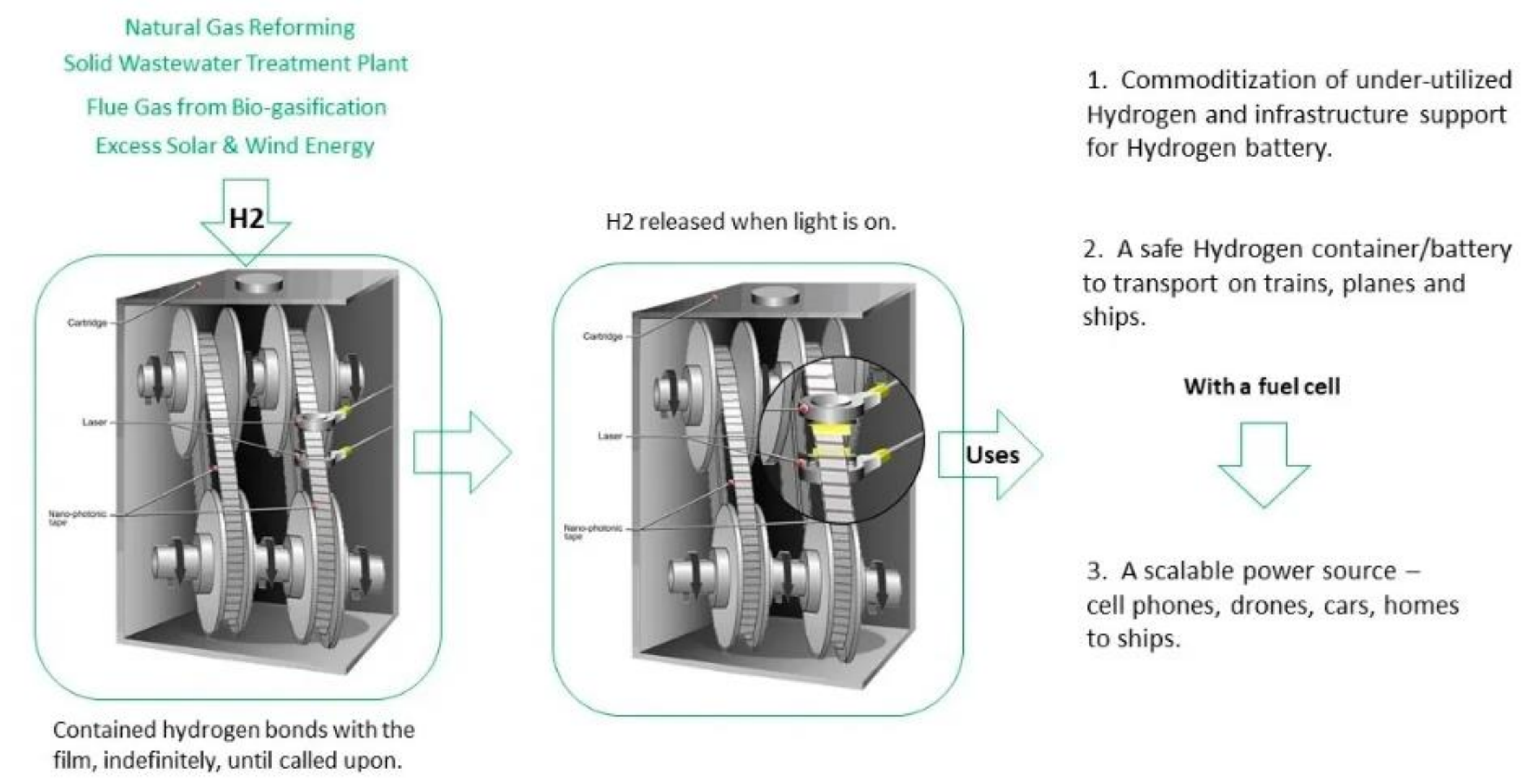
- **Unfavorable adsorption/desorption process:** requires high temperature (200-500°C) , and has slow desorption kinetics. Many efforts have focused on Mg-based hydrides in recent years to reduce the desorption temperature and to faster the re/dehydrogenation reactions. These can be accomplished to some extent by changing the microstructure of the hydride by ball-milling (mechanical alloying) with elements which reduce the stability of the hydrides and also by using proper catalysts to improve the absorption/desorption kinetics.
- **Not high enough storage capacity**: To date, rare earth-based material (rare earth metal, Ti, TiV system) is more mature in solid-state hydrogen storage. Among theses materials, TiMn-based material has already been applied in onboard hydrogen storage for FC buses. But as the metals have high atomic weight, the storage capacity is still in low level (~2.6%). To further increase the capacity, more efforts would be put on lightweight metal-based materials.
- **High material cost:** On the one hand, the raw material cost of hydrogen storage materials fluctuates greatly due to the price fluctuations of non-ferrous metal raw materials; on the other hand, the market for these materials is still small and hasn't been scaled up, which result in the higher manufacturing costs.

In view of the above-mentioned problems, it is particularly important to develop the R&D and application of reliable hydrogen storage materials.

Source: Courtesy of integralnewenergy.com

Hydrogen Storage Technologies > Carrier Technology: Plasma Kinetics

5. Carrier Technology: Plasma Kinetics (UNDER DEVELOPMENT & EVALUATION)



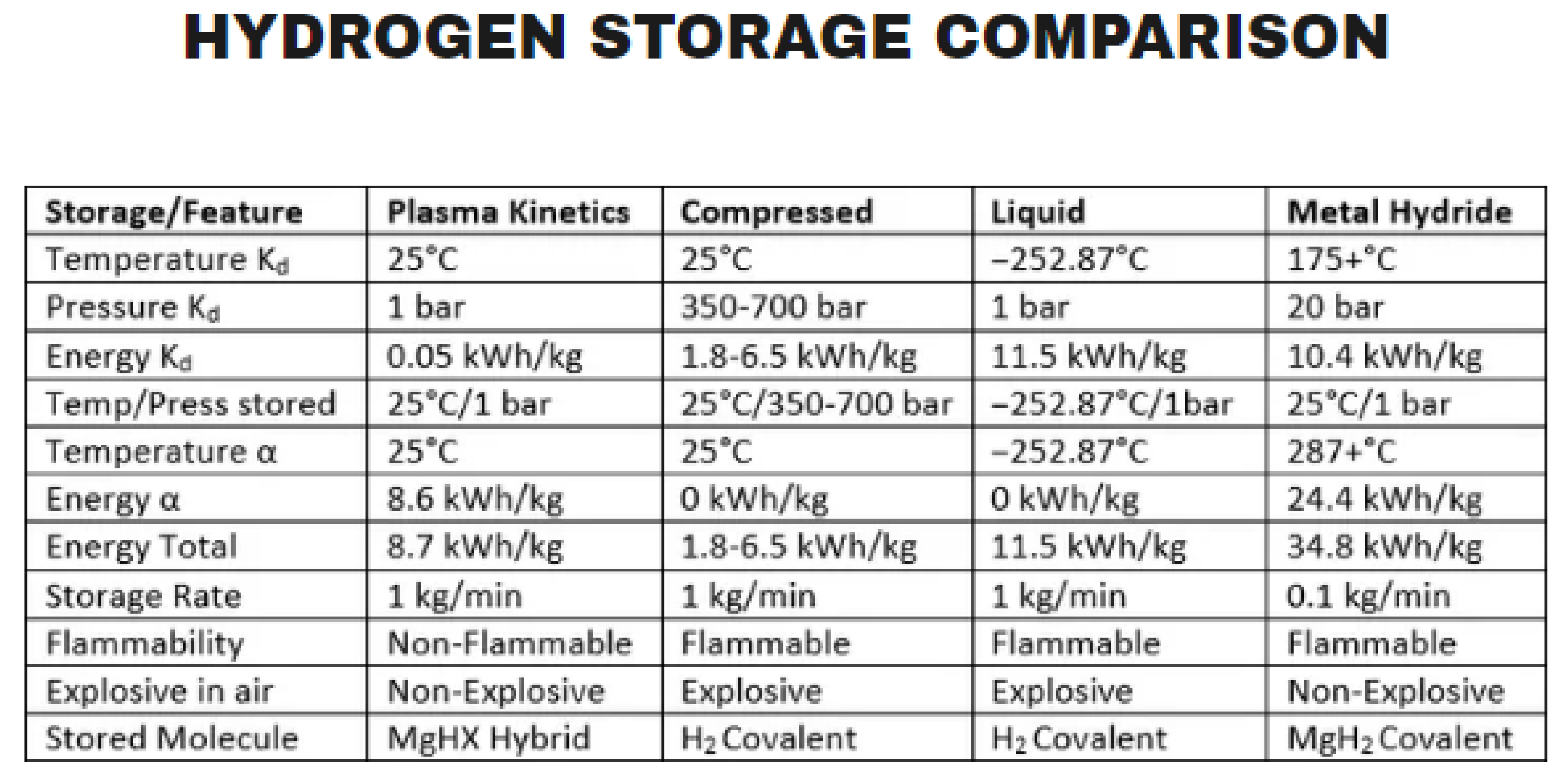
Contained hydrogen bonds with the film, indefinitely, until called upon.

1. Commoditization of under-utilized Hydrogen and infrastructure support for Hydrogen battery.
2. A safe Hydrogen container/battery to transport on trains, planes and ships.
3. A scalable power source – cell phones, drones, cars, homes to ships.

Source: Courtesy of plasmakinetics.com

Hydrogen Storage Technologies > Carrier Technology: Plasma Kinetics

5. Carrier Technology: Plasma Kinetics (UNDER DEVELOPMENT & EVALUATION)



HYDROGEN STORAGE COMPARISON

Storage/Feature	Plasma Kinetics	Compressed	Liquid	Metal Hydride
Temperature K_d	25°C	25°C	–252.87°C	175+°C
Pressure K_d	1 bar	350-700 bar	1 bar	20 bar
Energy K_d	0.05 kWh/kg	1.8-6.5 kWh/kg	11.5 kWh/kg	10.4 kWh/kg
Temp/Press stored	25°C/1 bar	25°C/350-700 bar	–252.87°C/1bar	25°C/1 bar
Temperature α	25°C	25°C	–252.87°C	287+°C
Energy α	8.6 kWh/kg	0 kWh/kg	0 kWh/kg	24.4 kWh/kg
Energy Total	8.7 kWh/kg	1.8-6.5 kWh/kg	11.5 kWh/kg	34.8 kWh/kg
Storage Rate	1 kg/min	1 kg/min	1 kg/min	0.1 kg/min
Flammability	Non-Flammable	Flammable	Flammable	Flammable
Explosive in air	Non-Explosive	Explosive	Explosive	Non-Explosive
Stored Molecule	MgHX Hybrid	H_2 Covalent	H_2 Covalent	MgH_2 Covalent

Source: Courtesy of plasmakinetics.com

Conclusions

(1) High-pressure gaseous hydrogen is currently the most mature and the mainstream method for hydrogen transportation

(2) Cryogenic hydrogen transportation has a relatively high hydrogen storage density and is in rapid development. The standardization work is ongoing, and civil cryogenic hydrogen projects are getting more attention. With the increase in the volume of hydrogen transported, its economy of scale will be highlighted.

(3) LOHC and Metallic Hydride are not yet commercialized.

- Some features of LOHC (easy to handle, easy to transport, chemically stable) make it not only promising medium for long-distance transport, but also for long-term storage.
- Although Metallic Hydride has some advantages (ambient storage condition), it is undeniable that more research should be done to overcome the drawbacks (low storage density, difficulty in hydrogenation/dehydrogenation) before it can be manufactured and commercialized.

(4) In the future hydrogen energy industry system, we expect renewable energy production to replace industrial by-product hydrogen as a clean and high-quality hydrogen source. Under this vision, we look forward to transportation method suitable for higher hydrogen storage capacity and for longer distance.

Credits

integralnewenergy.com
Hy Responder (European Hydrogen Train the Trainer Programme for Responders)
plasmakinetics.com

Thank you