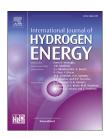


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Review Article

Is the H₂ economy realizable in the foreseeable future? Part II: H₂ storage, transportation, and distribution



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HIGHLIGHTS

- H₂ storage in compressed form is the commercially viable technology at present.
- Critical cost factors in H2 storage, transportation and distribution are provided.
- ullet Logistic flow of H_2 from storage points to various mobility applications is presented.
- H₂ transportation by road, pipeline and ocean is reviewed for large-scale application.
- Compressed H₂ transportation by road is the viable option for the automotive sector.

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ABSTRACT

The goal of the review series on the H_2 economy is to highlight the current status, major issues, and opportunities associated with H_2 production, storage, transportation, distribution and usage in various energy sectors. In particular, Part I discussed the various H_2 (grey and green) production methods including the futuristic ones such as photoelectrochemical for small, medium, and large-scale applications. Part II of the H_2 economy review identifies the developments and challenges in the areas of H_2 storage, transportation and distribution with national and international initiatives in the field, all of which suggest a pathway for establishing greener H_2 society in the near future. Currently, various methods, comprising physical and chemical routes are being explored with a focus on improving the H_2 storage density, capacity, and reducing the cost. H_2 transportation methods by road, through pipelines, and via ocean are pursued actively in expanding the market for large scale applications around the world. As of now, compressed H_2 and its transportation by road is the most realistic option for the transportation sector.

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Introduction

Large-scale energy generation from renewable resources will be required for a transition towards a net zero-carbon footprint society. H₂ is known to be a key component to enable the integration of large-scale renewables, and also to become a major energy carrier able to transport and distribute the energy throughout sectors and regions as well as acting as a buffer to improve the resilience of the energy systems. Part I of this series [1] is focused on H₂ production methods that will be available for massive and clean productions in the future energy scenario featuring H₂ as an energy vector in the residential, industrial, transportation, and commercial sectors [2].

For making the H_2 economy commercially viable, H_2 should be stored, transported, and distributed for power and/or heat generation on-demand for various applications [3]. A very recent publication highlights outlook on the future prospects and recent research on H_2 -based Energy Storage through the H_2 Technology Collaboration Program of the International Energy Agency [4]. Various studies have been conducted on the integration of renewable energy systems with H_2 storage as well; to achieve the net-zero-emission energy systems [5,6] and sustainable development goal [7]. With the H_2 utilization technologies (fuel cells) becoming more affordable, energy storage in batteries can be replaced through electrolyzers/ H_2 storage due to higher efficiency, reliability and performance. Hence, integration of the H_2 storage in the H_2 value chain

along with renewable energy sources such as solar, and wind is a promising approach [8]. Currently, the cost of the $\rm H_2$ system is higher compared to battery system but the recent research activities on the $\rm H_2$ value chain for various applications are expected to make them competitive by 2030 [5,9]. In Part II of the series, $\rm H_2$ storage, transportation, and distribution are reviewed in detail with a major focus on the technological and commercial point of view towards the $\rm H_2$ economy. In addition, the review provides the insight of intercontinental large scale $\rm H_2$ transportation.

In fact, H_2 could be distributed by blending (up to 15%) it with natural gas and using the existing infrastructure, with required modifications to the online monitoring for ensuring safety. Higher H_2 concentrations will require retrofitting or replacement of the existing infrastructure. The economic feasibility of a progressive H_2 deployment will become clear only if large-scale H_2 production, distribution, and transportation are adopted for various applications [10]. In this context, it is very critical for the energy industries, local and federal agencies, educational institutions and non-profit H_2 advocates/organizations to work together in establishing a robust storage and distribution systems for the seamless transition towards the H_2 economy.

The scope of Part II of the $\rm H_2$ economy review series can be visualized through the schematic representation in Fig. 1. Once $\rm H_2$ is produced in either small or large scales, the industrial and transportation applications depend on the storage and transportation/distribution capability. $\rm H_2$ can either be compressed or liquefied and stored for small and medium scale applications or transported through pipelines (or by truck or ship tankers) for large-scale applications.

H₂ storage methods

 H_2 can be stored either in compressed (350–700 bar) or liquefied (–253 °C) or solid forms for enhancing the gravimetric

density [11]. This section also discusses the advantages and specific issues about the H₂ storage options, the constraints related to materials, the important technological gaps, and the priorities and recommendations for further development.

As seen in Fig. 2, H₂ storage methods can be broadly classified into two, such as physical storage and material storage. While the physical storage system is based on the principle of compression and liquefaction, the material storage systems are many and offer a variety of utilization modes based on the service conditions.

Physical storage methods

Physical methods of H_2 storage are based on either compression or liquefaction or the combination of both.

Compressed

The most common and simple method of H_2 storage is in its natural form. Worldwide, the prevalent refueling stations adopt the gaseous storage under high pressure, which finds application in stationary, vehicular and bulk transportation [12]. Storing H_2 as high-pressure gas has the advantage of fast filling and high release rate, whereas the large space requirement and safety concerns are the main drawbacks of H_2 storage in high-pressure tanks. The compressed form in carbon fiber composite pressure vessels at pressures ranging from 20 to 100 MPa is used when lightweight capacity is needed, and in metal pressure vessels if high capacity is required [13,14]. Underground H_2 storage could also be a potential method and is discussed briefly in Section Seasonal storage at production and delivery sites.

Liquefied and cryo-compressed

Storing liquid H₂ achieves higher energy density per unit volume than compressed storage but the energy consumption is higher for liquefaction. Also, loss of H₂ due to the boil-off phenomenon in vehicular applications needs to be

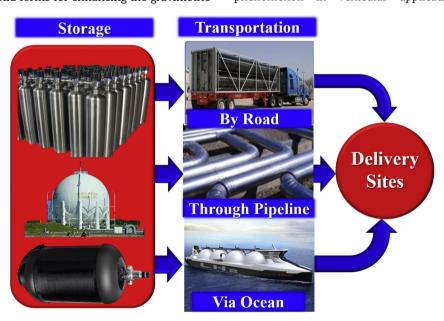


Fig. 1 – Schematic representation of the H2 storage, transportation, distribution and delivery showing the scope of the Part II of the review.

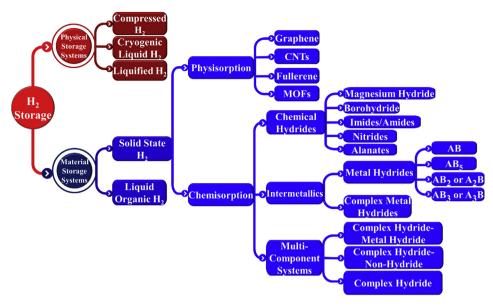


Fig. 2 – Classification of H₂ storage methods and materials.

minimized by insulating the container without any reduction in both the gravimetric and volumetric energy densities [15]. Cryogenic vessels are generally used for storing and transporting H₂ for medical as well as industrial applications. Liquefaction of H_2 at -253 °C is energy-intensive (40% of H_2 energy) compared to compressed H2 systems (10-15% of H2 energy) [16]. Storage at -253 °C is achieved by vacuum insulated inner pressure vessel with an external casing. Cryocompressed storage offers a synergy of both compressed gaseous H2 and liquefied H2 storage systems. While compressed H2 is stored at near-ambient temperatures, "cold" and "cryogenic" compressed H2 storage is carried out at a low temperature for realizing higher H2 densities. With a lower boil-off loss in liquefied H_2 storage, storage density 80 g L^{-1} can be attained [17]. The performance of liquid H_2 in terms of weight, volume, and cost are 2.0 kWh kg^{-1} , 1.6 kWh L^{-1} , and \$6per kWh, respectively, while those of various other storage technologies are given in Table 1 [18-22].

Material based storage

H₂ storage through chemical systems is one of the ways in effectively meeting various transportation applications. However, there is no single chemical compound meeting all the required properties. The anticipated storage solutions require a breakthrough in material properties. This can be achieved by innovation in basic research which is essential for technological advancement. The challenges demand commercially viable, higher H₂ storage capability, cyclic stability of the chemical systems that can be achieved by various smart nanoscale materials [23]. In order to increase the volumetric H₂ storage, solid-state organic hydrides have huge potential through physisorption and chemisorption. Alloy or complex-type materials are also expected to demonstrate high H2 storage capability. Carbonaceous materials are applicable, as they possess large surface areas to adsorb H₂, and their performance enhancement can be done by

H ₂ storage systems	Gravimetric (kWh kg ⁻¹)	Volumetric (kWh L ⁻¹)	Cost (\$ per kWh with 500,000 units per year)
Liquified	2.0	1.6	6
700 bar compressed (Type IV) [18,19]	1.4	0.8	15
300 bar compressed (Type IV)	1.8	0.6	13
Cryo compressed (500 bar) [20,21]	2.3	1.4	18
Metal Hydride (NaAlH ₄ /Ti) [22]	0.4	0.4	43
Sorbent (MOF-5, 100 bar, HexCell, LN ₂ cooling)	1.3	0.7	15
Chemical H ₂ Storage (AB- liquid)	1.5	1.3	17
2020 Target (DOE, USA)	1.5	1.0	10
2025 Target (DOE, USA)	1.8	1.3	9
Ultimate Target (DOE, USA)	2.2	1.7	8

techniques such as Kubas interaction, spillover effect, functionalization, and with alloying and incorporating additives [23]. Materials such as ammonia, methanol, methane, dimethyl ether or methylcyclohexane containing multiple H atoms can also serve as potential H_2 storage carriers, as long as the carbon required for their synthesis is sustainable. In addition, social acceptance as well as safety will be inexorable for commercializing the H_2 economy [24,25] with concurrent development of H_2 carrier materials and large scale storage technologies.

Physisorption

Physisorption is the physical bonding of H_2 molecules on the surface of an adsorbent by the weak van der Waals forces (binding energy: 10-100 meV) [26]. Physisorption happens quickly at low operating temperatures and does not encompass any chemical reaction. Large surface area and porous materials such as activated carbon, graphene, carbon nanotubes, C60 buckyballs, zeolites, and metal-organic frameworks are alternatives for physisorption.

Activated carbon is formed from carbonaceous source or biomass and it possesses an astonishingly large surface area (up to ~3000 m 2 g $^{-1}$) and a network of submicroscopic pores. Graphene is a monolayer containing sp 2 hybridized atoms of carbon with a thickness of ~0.34 nm and covalently bonded to three other carbon atoms in a honeycomb framework. The unique structure of graphene offers excellent physicochemical properties such as high specific surface area, superior mechanical strength, unparalleled thermal and electronic conductivities, and remarkable optical properties [27–29]. Morse et al. reported H $_2$ storage capacity of 3.2 wt % using hydrogenated graphene for demonstrating fuel cell operation [30]. Fullerene is the third allotropic form of carbon material after graphite and diamond. The most common fullerene molecule is C60, containing 60 carbon atoms.

Zeolites are crystalline, porous aluminosilicates in which the primary building blocks are TO_4 tetrahedron, where T indicates Si^{4+} or Al^{3+} cation. If there is silicon in the tetrahedron framework, the overall structure becomes electrically neutral. In the zeolite structure, Al^{3+} cations replace part of the Si^{4+} , leading to positive charge deficiency [31,32]. The large surface area of zeolite enables the adsorption of gases, which is used in the case of H_2 storage.

Metal organic framework (MOF) is a family of synthetic porous materials with metal ions or clusters linked to various organic ligands, for forming 1, 2 or 3D structures. They possess exceptionally high surface area and porosity that make MOFs more promising than zeolites or carbon nanostructures. When guest molecules are removed by heating under vacuum during the solvent exchange process, the MOFs porous structure can be obtained without the framework destabilization [33,34]. As a result, the H₂ molecules could adsorb by physisorption on the pore surface. In general, pore size, surface area, ligand structure, catenation, etc. are the major factors in determining the H₂ uptake by MOFs.

Chemisorption

In chemisorption, the adsorbate or vapor molecules split into atoms or radicals to form a chemical bond by sharing electrons with the adsorption site. Unlike physisorption, chemisorption involves a much stronger interaction and is difficult to reverse (Examples: metal, complex, and chemical hydrides) [35].

Chemical hydrides. In chemical hydrides, compounds of H₂ and non-metals, the bonds are formed by electron pairs sharing by atoms with comparable electronegativity. In the volatile non-metal hydrides, van der Waals forces hold together in the condensed state (Examples: B₂H₆, NH₃BH₃, NH₃) [36]. Chemical hydrides are gases or liquids with relatively lower freezing and boiling points. Boron forms an extensive series of covalent hydrides. Borohydrides or tetrahydroborates are ionic compounds $(M(BH_4)_n)$ with M^{n+} metal cations and BH₄ borohydride anions in a tetrahedral geometry. The borohydride ion is bound to the metal cation by bridging H2 atoms in three different ways, namely mono-, bi-, and tri-dentates with one, two, and three H2 bridges, respectively. Several metal hydrides such as magnesium hydride, magnesium nickel hydride, sodium aluminum hydride, and compounds such as borohydrates and alanates, are investigated for cyclic uptake and release of H2 [8]. Unfavorable thermodynamics and kinetic barrier of these metal hydrides needs to be further improved for their commercialization [37]. Polymeric materials and micro-glass globules are also attempted for the storage of H₂ [38]. Alanates are complex metal hydrides (M(AlH₄)x) with Mⁿ⁺ metal cations (Li⁺, Na⁺, K⁺, Mg²⁺, and Ca²⁺) and AlH₄ anions, bonded ionically. As seen from Table 2, the volumetric capacity of the solid state H₂ storage system has a linear trend as a function of the volumetric capacity of MHs. Evidently, the system based density could reach 50% compared to that of the MHs [12]. The MH properties and the tank design geometry are the key factors influencing the energy density of the H2 storage systems.

Intermetallic hydrides. H_2 can be chemisorbed on metals and intermetallic alloys with varying degrees of storage capacity. Alloys of the type A_2B , AB, AB_2 , and AB_5 are promising candidates, where A and B are metals. In the metal hydrides (MH), the bonds (metal to hydrogen) are covalent but some hydrides are formed with ionic bonds. There are H_2 filling stations using MHs with low-pressure H_2 (absorption capacity: ~3 wt %) [39]. The automotive industry is not trying for MH based systems and decided to proceed with high-pressure H_2 tank (70 MPa). However, the MH systems for vehicles can solve the issues such as safety, development of cost effective refueling

Table 2 — Theoretical gravimetric and volumetric capacity of various alloys and their volumetric capacity of the system.

МН			Volumetric capacity of the system (kg H ₂ per m ³)
Hydralloy	1.6	115	57
NaAlH ₄	7.3	93	46
LaNi ₅	1.6	115	57
LiBH ₄	18	122	61
MgH_2	7.7	110	55

Table 3 — Thermodynamic properties of most common intermetallic compounds.			
Formula	x in MH_x	H ₂ equilibrium pressure, MPa (T in K)	Enthalpy of hydride formation, kJ . mol^{-1}
LaNi ₅ [41]	6.3	0.1 (285)	-31.8
MmNi ₅ [42]	6.3	1.3 (293)	-30.0
LaNi ₅ [43]	6.0	0.37 (313)	-31.2
LaNi _{4.8} Al _{0.2} [44]	6.0	0.2 (323)	-35.0
CaNi ₅ [12]	6.0	0.08 (313)	-33.1
LaNi ₄ Al [45]	4.0	0.2 (453)	-53.0
Mg ₂ Ni [46]	4.0	1.15 (633)	-62.7
ZrMn ₂ [47]	3.5	0.2 (374)	-44.4
Ti _{1.2} Mn _{1.8}	2.5	0.7 (293)	-28.0
TiFe	2.0	0.7 (313)	-28.1
Mg	2.0	0.9 (638)	-76.2
TiCo	1.4	0.1 (403)	–57.7

infrastructure and other operational hurdles [40]. Table 3 provides $\rm H_2$ storage capability (number of hydrogen atom per formula unit), equilibrium pressure, and enthalpy of formation for various metal hydride systems studies in the literature [12,41–47]. Among various systems, the La based $\rm AB_5$ intermetallic compounds have the highest $\rm H_2$ storage capability, offering safety and reliability for portable applications, in-house and in-board storage.

Complex metal hydrides. In complex metal hydrides, Mⁿ⁺ metal ion forms ionic bonding with molecular hydride anion and the hydrogen and the second metal or metalloid atoms M' are bonded covalently [48]. The complex metal hydrides (Mx-M'vHn) have alkali or alkaline metal M (Ca, Na, K, etc) and M' (Al, Li, Na, etc) is a metal in the hydride anions $((AlH_4)^2)$ (LiAlH₆), (NaAlH₆)²⁻, etc). Several, binary or pseudo-binary intermetallic compounds based hydrides in H2-storage containers have been studied for various applications including heat pumps, high-performance Ni-MH batteries, etc [49], with facile absorption/desorption characteristics. Among various intermetallic compounds, Ti-based systems operate effectively for H₂ storage under moderate conditions [50]. The H₂ absorption/desorption leads to interstitial hydride formation through the following reaction pathways. Initially, the H2 molecule is adsorbed on the metal (or alloy) surface and gets dissociated to form two atoms. Then, the hydrogen atoms diffuse to the bulk to occupy the metal (or alloy) sub-lattice's interstitial sites, leading to a 20-30% expansion of the sublattice. A self-trap mechanism of hydrogen occupying the interstitial sites has been proposed, based on the elastic energy of the lattice and the enthalpy of hydride formation [51].

Multicomponent. Multicomponent H_2 storage systems are also known as reactive hydride composites consisting of more than one phase in the H_2 loaded state, which may be simple physical mixtures or a composite where one phase represents a host matrix. During dehydrogenation, both phases react leading to often the dehydrogenated products consisting of more than one phase. The design of novel multicomponent mixtures for H_2 storage focuses on the mixtures of materials from two distinct classes such as reversible and irreversible. High capacity multicomponent hydrides consist of complex hydrides (borohydrides, alanates or amides), metal hydrides

(LiBH₄-MgH₂ or LiAlH₄-LiNH₂), and other chemical hydrides (LiNH₂+NH₃BH₃) phases [52].

Liquid organic. Liquid organic H2 carriers (LOHC) are the unsaturated organic compounds (cycloalkanes, N-heterocyclanes, formic acid, etc) for storing a large amount of liquid H₂ indirectly. The LOHC research is limited to cycloalkanes (6-8 wt % H₂) [53], heterocyclic aromatic compounds or N-Heterocycles (N-Ethylcarbazole [54,55], dibenzyl toluene (6.2 wt % H₂) [56], etc) with various compounds as a semantic candidates for storage and possessing a higher overall energy efficiency compared to chemical storage options [57,58]. Formic acid is also one of the most promising H2 storage candidates with 4.4 wt % H2 capacity [59]. In general, the dehydrogenation of cycloalkanes (catalysts: Ni, Mo, and Pt; 300–400 °C) is extremely endothermic (63–69 kJ mol $^{-1}$) compared to other LOHCs [43-45]. The gravimetric and volumetric H_2 storage densities are 6.1 wt % H_2 and 43 kg H_2 per m^3 , respectively. Replacing some of the carbon atoms of hydrocarbons by heteroatoms (N, O, etc) lead to improved reversibility and reduced the temperature requirement for dehydrogenation/hydrogenation [60]. Dodecahedron-N-ethyl carbazole has been reported to store a large amount of H₂ (5.8 wt %) [61]. The catalysts based on Ru and Rh improve the hydrogenation selectivity to 97% at 7 MPa and ~140 °C. Formic acid was reported to be the H2 storage material in 2006 by Swiss researchers, generating CO free H2 in a very wide pressure range (0.1–60 MPa) [62]. Formic acid stores 4.3 wt % H₂ at ambient temperature and pressure, nevertheless various important parameters such as the toxicity are limiting factors. Therefore, there is intense need for the development of environmentally benign, cost effective, easy to transport, convenient and reversible hydrogen storage systems. In this regard, Zou et al. reported ethylene glycol based LOHC system with a proven H₂ storage capability of 6.5 wt % and further development is in progress considering various key practical aspects [63]. LOHC could be one of the suitable candidates for terrestrial transportation and aviation industry [64], since it is economically advantageous as the existing infrastructure can also be employed for its transportation and delivery [65]. Currently, the major research and development focuses on the development of organic systems, which can generate H2 at

Table 4 – Overview of DOE targets towards solid-state H	2
storage [66].	

Storage parameter	By 2020	Ultimate
Gravimetric capacity (kg H ₂ kg ⁻¹)	0.055	0.075
Volumetric capacity (kg $H_2 L^{-1}$)	0.040	0.070
System cost (\$ kg ⁻¹ H ₂)	333	266
Operating temperature (°C)	40-60	40-60
Delivery temperature (°C)	40-85	40-85
Cycle life (cycles)	1500	1500
H ₂ fill time for 5 kg (min)	3–5	4-5

relatively higher pressure at ambient temperature using less expensive catalysts with a reversibility of >97%.

H₂ storage challenges

The US-DOE has established the targets for an on-board $\rm H_2$ storage system in terms of gravimetric/volumetric capacity, material cost, operating temperature, desorption temperature, and reusability of $\rm H_2$ storage medium for automotive applications and are shown in Table 4 [66]. A large variety of $\rm H_2$ storage materials such as borohydrides, chemical hydrides, metal hydrides, complex hydrides, zeolites, MOFs, etc. have been investigated for their applicability and efficiency as potential $\rm H_2$ storage materials. The ultimate aim is to develop a lightweight and compact $\rm H_2$ storage medium for meeting the DOE targets.

The technical targets for the onboard H_2 storage in the case of light-duty fuel cell vehicles (FCVs) are summarized in Table 5 [67].

The R&D gaps for H_2 storage (liquid, solid, and gaseous forms) with respect to the technological status, best options that have to be addressed are given in Table 6. Evidently, the energy required to store H_2 is a major challenge in all three modes (gas, liquid and solid), even though commercial systems are available for targeted applications.

H₂ storage, transportation and distribution

 $\rm H_2$ production can take place in large and centralized plants from various energy resources [1]. However, transferring the $\rm H_2$ from the production site to the delivery site is challenging, especially when the energy source is in a remote area. Further, $\rm H_2$ production and user demand will vary with time. Therefore, the seasonal storage of $\rm H_2$ in large quantities at production and the closest $\rm H_2$ delivery sites will help to regulate the consumption and production processes.

In general, the H_2 supply chain includes three main stages: (i) production and bulk/seasonal storage at the production site, (ii) transport, and (iii) bulk storage/seasonal storage at the delivery site and delivery to the end-user. Fig. 3 provides the logistic flow of transportation by tank and tube trailers of liquid and compressed H_2 to the delivery sites [66,68]. The H_2 pressure handled at each stage is different and hence the

Parameter	Unit	2020	2025	Ultimate
System capacity (Gravimetric)	kWh/kg	1.5	1.8	2.2
	(kg H ₂ /kg system)	(0.045)	(0.055)	(0.065)
System capacity (Volumetric)	kWh/L	1.0	1.3	1.7
	(kg H ₂ /L system)	(0.030)	(0.040)	(0.050)
Storage system cost	\$/kWh net	10	9	8
• Fuel cost	(\$/kg H ₂)	(333)	(300)	(266)
	\$/gge at pump	4	4	4
Durability/Operability:	°C	-40/60	-40/60	-40/60
Operating ambient temperature	°C	-40/85	-40/85	-40/85
Min/max delivery temperature	Cycles	1500	1500	1500
Operational cycle life (1/4 tank to full)	Bar	5 and 12	5 and 12	5 and 12
Minimum and Maximum delivery pressure from storage system	%	90	90	90
Onboard efficiency	%	60	60	60
"Well" to Powerplant efficiency				
Charging/discharging rates:	Min	3-5	3-5	3-5
System fill time	(g/s)/kW	0.02	0.02	0.02
• Minimum full flow rate (e.g., 1.6 g/s target for 80 kW rated fuel cell power)	(g/s)/kW	0.004	0.004	0.004
Average flow rate	S	5 and 15	5 and 15	5 and 15
ullet Start time to full flow at 20 °C and -20 °C	S	0.75	0.75	0.75
• Transient response at operating temperature 10%–90% and 90%–0%				
(based on full flow rate)				
H ₂ quality (from storage)	% H ₂	Meet or ex	ceed SAE J271	9
Dormancy time target (minimum from initial 95% useable capacity)	Days	7	10	14
Boil-off loss target (maximum reduction from initial 95% useable capacity after 30 days)	%	10	10	10
Permeation and leakage, Toxicity, and Safety	_	Meet or ex	ceed SAE J257	9
Recycleability		According Directive 2	to End-Of-Life 000/53C	e Vehicle

Table 6 — H ₂ storage	technology status, options and R	&D challenges and opportunities.	
Storage Mechanism	Status	Options	R&D Challenges and Opportunities
Gaseous H ₂	Commercially available, not too expensive	C-fiber composite vessels (6–10 wt $\%$ H $_2$ at 350–700 bar)	Fracture mechanics, safety, compression energy, reduction in volume, codes and standards.
Liquid H ₂	Commercially available, but expensive	Cryogenic insulated Dewar (~20 wt $\%$ H ₂ at 1 bar and -253 °C)	Energy intensive, dormant boil off, safety, codes and standards.
Solid $ m H_2$	Smaller units available, but exorbitantly expensive	Potential options: Rechargeable hydrides, chemical hydrides, carbon, and other high surface area materials.Best option: Metal hydrides (potential for > 8 wt% H ₂) Performance enhancement by catalysis, nano scaling, compositing or ionic substitutions and functionalization by heteroatom substitution.	Weight, lower desorption temperatures, higher desorption kinetics, unfavorable thermodynamics, recharge/ refueling time and pressure, thermal management, pyrophoric, cycle life, container compatibility, optimization, codes and standards. And high cost

supporting technologies such as gaseous compressors, pumps, and pressure-reduction stations are required in each stage. Since H_2 tends to cause embrittlement of metals (H_2 -assisted fracture), especially at higher pressures, more attention needs to be paid to the materials' compatibility. H_2 has very low ignition energy of around 0.02 mJ to start the

combustion reaction with 4–75 vol % H_2 in the air and even lower in the oxygen. Due to a higher diffusion coefficient of H_2 in air, 0.61 cm²/s (0.05 cm²/s for gasoline and 0.16 cm²/s for methane), proper safety measurements should be implemented in each stage of the H_2 supply chain for ensuring safety. Today, the industry is already handling H_2 for many

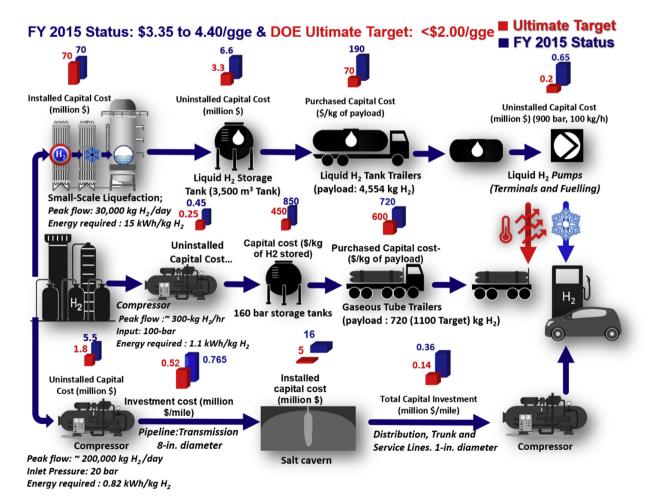


Fig. 3 - H₂ storage and transportation - a logistic flow along with cost targets, for mobility applications [66].

purposes on a large-scale including refineries or ammonia production. However, when it comes to handling H_2 at a broader scale, important points to consider are how H_2 can be transported efficiently, on time and safely. In addition, optimization models are important for infrastructure development, using the H_2 supply and demand, and evolution of the H_2 supply chain network in the near term, midterm and long terms [69]. As H_2 distribution is new to the energy companies and existing infrastructure, it will be necessary for them to find good solutions for handling large quantities of H_2 in order to be competitive in the future energy market. Since the market transformation is one of the main challenges therefore, enormous interdisciplinary opportunities and jobs emerge on the horizon for the associated community towards realizing H_2 economy [70].

Seasonal storage at production and delivery sites

As discussed in earlier sections, H2 could be stored in different states (gaseous, solid, liquid, and dissolved in the organic solvent). Among them, storing H2 in a gaseous form is simplest in terms of infrastructure required and it is also the best-developed method at present [71]. The only equipment required for gaseous H2 storage is a compressor and a pressure vessel [72,73]. For smaller quantities, the H2 gas is compressed (20 MPa) and stored in 50 L cylinders with end domes, similar to those used for any process gases [71]. The cylinders can be stored at environmental temperatures between -50 and 60 °C. Usually, the cylinders are made of steel which is cheap, and they can withstand H₂ pressures up to 200 bar, holding 0.9 kg of H₂. This type of cylinder is useful in small scale applications where low amounts of H2 are required. For storage of larger amounts, H2 can be compressed at 165 bar and stored in spherical vessels with a capacity of about 2000 m³ holding 29,700 kg of H₂. This is equivalent to the electrical energy of 989 MWh (41 MW for 24 h) with an energy density of 33.33 kWh· kg^{-1} H₂. The power required for a city with a population of 1 million is 1500 MW for countries such as the Nordics, USA, and Australia.

Therefore, the equivalent need is around 37 spherical vessels of 2000 m³ capacity, whereas a storage vessel with the same capacity of 2000 m³ can hold up to 142,000 kg H₂ in liquid form at -253 °C and 1.013 bar. This is 4.8 times more than for compressed H₂ gas at 165 bar. The largest liquid H₂ tank is spherical (diameter: 20 m; volume: 3800 m³) for storing ~230,000 kg, for space shuttle application in the USA [71]. This tank could provide electrical energy of around 319 MWh. A small percentage of stored liquid H_2 will be lost (2-3% in smaller and ~0.2% in larger and smaller containers per day, respectively) due to evaporation (boil-off) [71]. Furthermore, there is an increased risk of vessel failure since the materials become brittle at low temperatures. Besides challenges in maintaining the liquid vessels, it is also very costly to install, along with other concerns such as lack of technical manpower for commissioning and maintenance. Consequently, the energy price will be high and not suitable for commercial applications.

Another possibility to store H_2 in larger volumes at a reduced price is storing underground such as in salt caverns, aquifer, salt domes, and human-made cavities [74]. The optimal seasonal storage pressure in a cavern is generally 175–200 bar, whereas the capacity is in the range of million m^3 . This is a much more efficient, low-cost, and flexible system than installing many small storage vessels. H_2 produced continuously from wind/solar energy can be stored underground in huge quantities. The stored H_2 can later be transported whenever there is demand in the market facilitating the demand and supply process continuously. This is safer than working in smaller batches where there is a risk of running out of H_2 in the storage. Caglayan et al. [75] estimated

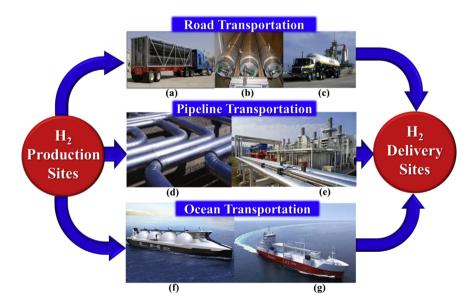


Fig. 4 - (a) Compressed H2 in Tube-Trailers, (b) Metal hydrides H2 storage, (c) Liquid H2 storage, (d and e) H2 transportation via pipeline, and (f and g) LH2 or LOHC transportation via ocean.

the potential of H_2 storage in salt caverns for Europe to be 84.8 PWh_{H2}, with Germany having ~40%.

Pure $\rm H_2$ gas has been stored in three caverns in Teesside, UK, since 1972 operated by Sabic Petroleum [76]. The volume of each cavern is about 70,000 m³ at 24 bar. The possible working gas capacity is 0.83 million kg, which is equivalent to ~1.3 GWh. There are also two caverns for storing $\rm H_2$ in the USA at Clemens and Moss bluff with volumes of 580,000 and 566,000 m³, pressure 70–135 bar, and 55–152 bar operated by Conoco Phillips and Praxair, respectively [76]. These caverns can store 2.56 and 3.72 million kg $\rm H_2$ with the energy equivalent of 3555 and 5166 MWh, respectively. This is enough for powering a city with one million people in the USA. However, storing $\rm H_2$ underground is demographically limited, as it is difficult to find suitable underground storage places near utility sites.

Transport

 $\rm H_2$ can be transported in gas, liquid, or metal hydrides form via road, pipeline or ocean. Compressed $\rm H_2$ gas can be transported from site to site in small quantities and short distances [77]. For long distances and a large amount of $\rm H_2$, using pipelines could be a better method. Liquid $\rm H_2$ can largely be transported over long distances via road or ocean, while Low-pressure $\rm H_2$ stored in metal hydrides can only be transported in a small quantity over a short distance.

Road transport

Truck. Trailers that are customized to carry stacked long gas cylinders as shown in Fig. 4a are called tube-trailers [68]. The storage pressure range for each cylinder is from 200 to 300 bar and is currently limited to a maximum 250 bar by the Department of Transportation, USA [78]. Trucks hauling these tube-trailers are currently used by industrial gas companies to transport compressed H_2 gas over short distances (200–300 km), and a trailer can carry from 2000 to 6200 m^3 H_2 [68]. The amount of H_2 carried is thus in the range of 180–540 kg, depending on the number of tubes. This represents 1–2% of the total mass of a truck of ~40 tons. Current trailers utilize Type 1 cylinders with ~1 wt % H_2 storage capability due to the heavier steel. Composite materials based vessels can store ~550 kg of H_2 at 250 bar, thus up to 720 kg of H_2 can be transported per trailer [78].

Metal hydrides based containers can be used for transporting H_2 by directly loading onto a truck or railcar (Fig. 4b) to

the customer/end-user sites, where it can be exchanged with the empty hydride containers [73,79,80]. The advantage of this transportation method is that the existing logistics infrastructure can be used where there is no need for using pressure for transportation and storage. Further, the hydrides require heat to release H_2 , and the chance of accidental H_2 release is therefore minor. Thus, H_2 stored in metal hydrides is less hazardous to transport compared to compressed H_2 or LH_2 transportation. However, the H_2 stored in this system has low gravimetric densities (1–7 wt %), and it will, therefore, be very expensive to transport.

As described above, the LOHC technology enables H_2 storage under ambient conditions and hence high pressure or highly-insulated tanks are not required [81]. In this context, the LOHC can use the currently existing transportation mode for fossil fuels such as road oil tankers, tank trucks, pipelines, rail trucks, tanker ships, etc [82]. However, the storage density of H_2 in LOHC is 6–8 wt %, therefore, the net storage capacity is still a major controlling factor. Furthermore, unlike a gasoline tanker, the LOHC trailer has to be returned to the chemical plants for catalytic hydrogenation [82].

Liquid H2 tankers. Currently, trailers customized to carry a single long cylinder, otherwise called tankers (Fig. 4c) are used to transport the LH₂. The trucks hauling the tankers with LH₂ are referred to as cryogenic tanker trucks or liquid tanker trucks. Liquid tanker trucks operating at atmospheric pressure have volumetric capacities of about 50,000-60,000 L and can transport up to 4000 kg H₂ with a truck mass of ~40 tons, which represents ~10 wt % of the total mass of the truck [68]. The particulars of road H2 delivery are given in Table 7 [83] and shows that LH₂ tanker trucks can transport 10 times more H₂ in terms of weight capacity than the tube-trailers with compressed H₂. This transport mode is thus more economical than transporting H2 in gaseous form. H2 storage capital costs and operating costs are given in Table 8 [83]. Transporting H₂ in liquid form requires a liquefaction plant; which is capitalintensive, in addition to the liquefaction process being costly. Furthermore, the liquefaction process, the transport time and the utilization time (end-use or delivery time) must be timely scheduled to avoid excessive H2 boil-off. The H2 evaporation rate depends on the container size/shape/insulation and time of storage and is typically of the order of 0.2% per day for a 100 m³ container [68]. However, the H₂ boil-off may not be an issue if the storage time is not longer than a week or two.

Table 7 $-$ Road H ₂ delivery estimations [84].			
	Cryogenic tanker tru	ick Tube trailer	
Load (kg)	4000	300	
Net delivery (kg)	4000	250	
Load/unload (h per trip)	4	2	
Boil-off rate (% per day)	0.3	_	
Truck utilization rate (%)	80	80	
Truck/tube (\$/module)	450,000	100,000	
Undercarriage (\$)	60,000	60,000	
Cab (\$)	90,000	90,000	

Table 8 — Capital o	cost (\$) and o	perating cost (energy) for H ₂
	Capital cost (\$)	Operating Cost (kWh/kg)
Compressor Compressed Gas Vessel	1000/kW 1323/kg	2.2
Liquefier Dewar Metal Hydride Underground	44100/kg/hr 441/kg 2200/kg 8.80/kg	10 – 6.46 (Hydride heat of reaction) –

Kawasaki Shipbuilding Corporation, Japan has demonstrated the performance of LH $_2$ containers at various stages, and the first public road test took place in January 2005 in Amagasaki-Tokyo Public Road [85]. A container carrying approximately 6000 L of liquid H $_2$, only half of the container's capacity, was transported along a 600 km route from the H $_2$ liquefaction site in Amagasaki City, Hyogo Prefecture, to the H $_2$ fuelling station in Koto-ku, Tokyo. The amount of liquid H $_2$ lost due to evaporation was limited to only 0.7% per day. Kawasaki is currently developing containers for LH $_2$ transportation with the ultimate goal of lighter weight, higher insulation efficiency, and lower cost.

Pipeline

Pipelines (Fig. 4d—e) are the most effective ones for transporting and distributing gaseous H_2 in a large scale continuously (tens of thousands of m^3 per hour). A number of commercial H_2 pipelines are currently used in refining and chemical industries with large amounts of H_2 requirements for chemical processing. The length of the pipelines ranges from less than a km to several hundreds of km [68]. Typical operating pressures are 10-30 bar with flow rates of 310-8900 kg/h [73,86,87]. The first H_2 pipeline reported to be in operation was opened in 1939 in Germany and was 210 km long, carrying 8900 kg/h of H_2 through a 250 mm pipeline operating at 20 bar [86]. The longest H_2 pipeline owned by Air Liquide is 250 miles, from France to Belgium [86]. The USA has a total of >1500 miles of H_2 pipelines, mostly in the Gulf Coast and the Great Lakes areas [73,86,88].

The total H₂ network in the world is estimated at around 16,000 km and mostly situated in the USA, Canada, and Europe. Overall, the H₂ pipeline lengths are tiny when compared to the worldwide natural gas transport pipeline system, which exceeds 2,000,000 km [68]. A way to expand the H₂ network would, therefore, be to employ the available natural gas pipeline network. Currently, there is a project called H21 for the conversion of UK gas networks to carry 100% H2. The gas distributor Northern Gas Network launched the H21 Leeds City Gate report in July 2016 and proposed that it is techno-economical to convert the natural gas network of Leeds, UK to carry 100% H₂. Currently, 83% of domestic homes in Leeds use natural gas for heating and cooking. The design incorporates a 1025 MW H2 production facility via steam methane reformers located at Teesside, a 700,000 MWh interseasonal storage in salt caverns in the Humber region and around 4000 MWh intraday storage in salt caverns in Teesside [89]. The total cost proposed for Leeds including H₂ production and storage, all associated infrastructure and appliance conversions in the region is £ 2 billion [89]. Cerniauskas et al. [90] evaluated the reassignment option of natural gas pipeline network for H₂ delivery in Germany, which will reduce the H₂ delivery cost by 60%. The pipelines for natural gas are constructed of steel and can withstand a maximum of 30 bar for H₂. However, it is not clear whether the components (gaskets, fittings, etc) used for natural gas pipelines can withstand H2 diffusion [90,91].

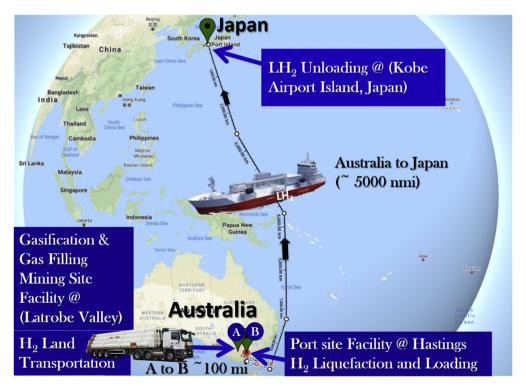


Fig. 5 – Transportation of LH₂ from Australia to Japan via ocean.

Table 9 — Specifications of tanker.	of Kawasaki's liquefied H ₂
Tank type	Double shell spherical tank
Ship type	Wave piercing semi-SWATH
Cargo capacity	200,000 $\text{m}^3 \text{ (} -253 ^{\circ}\text{C, 0.071 t/m}^3\text{)}$
Length	About 345.00 m
Breadth	64.00 m
Depth	26.00 m
Draft	14.00 m
Main engine	H ₂ burning boiler + Steam turbine
MCR	2 × About 40,000 PS (29,400 kW)
Propulsion system	4 × About 20,000 PS (14,700 kW)
	Waterjet pump
Service speed	About 25 knots
Boil-off rate	About 0.4%/day

Ocean transport

Renewable energy and fossil resources are limited in countries like Japan to produce H2 in larger quantities. Instead, intercontinental transport of H2 in liquid form can be performed using ships similar to the ones used for natural gas. In 2014, Kawasaki along with Iwatani and J-power initiated a project to establish a supply chain model for marine transportation of LH₂ (Fig. 4f) [92]. The idea is to transport H₂ from Australia produced by gasification of brown coal using a LH2 tanker (Fig. 5) with the specifications given in Table 9 [92,93]. The main challenge for this supply chain model is keeping the LH₂ below its boiling point of -253 °C. A double-shell tank was designed with a vacuum maintained in the space between the inner and outer shells. However, the conventional "suspension structure" to support the double-shell tank did not provide sufficient strength to withstand the pitching and rolling on the ocean. In addition, the heat insulation of the tank was initially too low. New tank support methods and materials satisfying both strength and heat conduction requirements have been proposed by the CO2-free H2 Energy Supply-chain Technology Research Association (HySTRA) in Japan and demonstrated that construction of a liquid H2 tanker is technically feasible. Indeed, the world's first liquid H2 tanker was finished in 2019 in Japan [93].

Moss Maritime, a design and engineering services company, has developed a design for a liquefied $\rm H_2$ tanker vessel along with Equinor (Wilhelmsen and DNV GL group) (Fig. 4g) [94]. The LH₂ tanker vessel has ~9000 m³ storage capacity incorporating a cargo containment system for minimizing boil-off along with stringent safety gadgets, for merchant ships and ocean transport. This is an important milestone for ocean transport of LH₂.

Once the market for H_2 grows, the number of developments, demonstration projects and feasibility studies initiated by big energy corporations will also increase. Along with specialized ships with appropriate tanks, port facilities should be planned and built, or the existing facilities and infrastructure should be modified for storing and handling LH_2 . As an alternative, the ocean transport and supply chain by means of LOHC has also been proposed, where demonstration plants (50 Nm³/h H_2) have been operated by Chiyoda Corporation, Japan using toluene and methylcyclohexane. Once the trade-in H_2 is established for large scale operation, these ideas can be realized.

Distribution

The H₂ delivery sites will have different designs depending on how the H₂ is delivered (mode of transport and physical state of the H₂), H₂ demand, where the station is located and the end-users [95]. For example, the design of H₂ refueling stations (HRS) for FCVs varies depending on the mode of H₂ delivery. If the delivery mode is gaseous H2 by tube trailer or cylinder racks, the HRS involves components such as seasonal H2 storage, intraday H2 storage tanks (tube trailer/tank/cylinder racks), compressors, refrigerators, and dispensers as shown in Fig. 6. In addition, the HRS has diverse operational parameters that will vary for each application. The refueling station pressure depends on the type of vehicle; cars refuel at 700 bar, while heavy-duty vehicles (buses and trucks) and light-duty vehicles (forklifts) refuel at 350 bar. Therefore, a compression unit will be part of the HRS site to increase the pressure from 200/300 to 450 and finally to 850 bar. H₂ from highpressure tanks will then be delivered to 350 or 700 bar dispensers through refrigerator units to provide enough cooling. The dispensable capacity of today's H2 stations is typically just

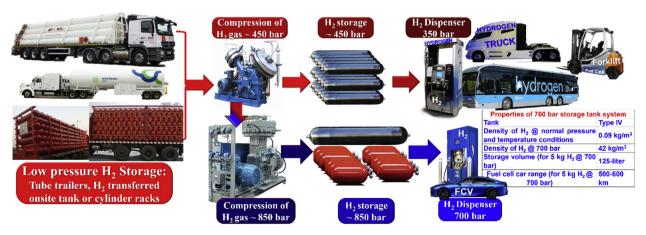


Fig. 6 – The process of low pressure to high pressure H₂ dispenser.

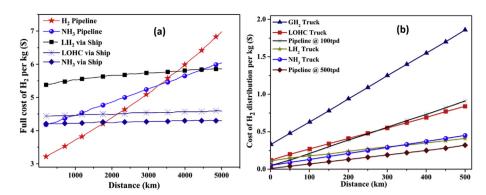


Fig. 7 – (a) Transportation and distribution cost for longer distances, and (b) distribution cost for shorter distances, by various modes as projected for 2030.

under 200 kg per day, which is sufficient to fill approximately 50 light-duty vehicles [96]. Such an amount of H_2 can be stored in a parked trailer or tank with a capacity of 2000–6000 m³.

If the demand for $\rm H_2$ increases, it is also possible to deliver $\rm H_2$ by pipeline. The Torrance Shell $\rm H_2$ station in California, USA is one of a few stations in the world connected to an existing underground $\rm H_2$ pipeline [97,98]. Air Products operates the $\rm H_2$ gas pipeline in Wilmington and Carson. The $\rm H_2$ gas is cleaned by palladium purifiers before transferring to high-pressure $\rm H_2$ storage tanks. Pipeline stations are expected to be economically attractive for delivery to residential use and industries.

If the delivery mode is liquid H_2 by tanker trucks, special safety measures should be given during the withdrawal of LH_2 from the tanker. This would require safety relief devices in a closed system, for eliminating the possibility of flammable atmosphere or an explosive liquid air and LH_2 mixture [99]. He gas can be used for purging as LH_2 can solidify if N_2 is used, causing plugging and possible rupture of the transfer line/ storage container [99]. Today's LH_2 stations typically have the ability to dispense around 350 kg/day which is equal to about 90 light-duty vehicles per day [96].

The choice of transporting and distributing $\rm H_2$ on an economical perspective (full cost) varies based on the distance and quantity, as projected for the year 2030 [100]. For longer distances (>1000 km), transporting $\rm H_2$ through pipeline and ship is the potential option. Evidently, transporting gaseous $\rm H_2$ by pipeline is the economical method up to ~1800 km (Fig. 7(a)) and the LH₂ by ship is the least expensive option for distances > 3500 km. In fact, the cost could be lower if the $\rm H_2$ carrier is either ammonia or LOHC. However, process cost (\$1 per kgH₂) for extracting $\rm H_2$ from ammonia or LOHC will make the overall cost higher and returning the empty ships will also make the logistics more complex.

For shorter distances (<500 km), specifically for local distribution, carrying LH_2 or ammonia by trucks is the viable option (Fig. 7(b)) [100]. If the demand increases, H_2 through pipeline is the best mode of transport, even for shorter distances. In addition, the choice of transport mode also depends on the required H_2 form (gaseous or liquid) at the utilization end. Apart from handling difficulties, transportation of LH_2 or LOHC is also economically attractive through trucks.

Conclusion

Part II of the series on H₂ economy review examined various H₂ storage and distribution methods available in the market and their choice from the perspective of economic viability and safety. Storage and distribution are key components in a future H₂ economy, once green H₂ production methods are well developed (covered in Part I of the review series). Both the energy density (volumetric and gravimetric) and operating cost for H2 storage and transportation play a critical role in distribution to the end-users. In the current scenario, H2 in compressed form and transportation by road is the most realistic option for the early-stage transportation sector. Once the number of end-users increase, both on the residential as well as industrial, centralized storage, and distribution methods such as underground storage and continuous supply through the pipeline will take effect. For realizing the H_2 economy, mathematical modeling for techno-commercial aspects, technological development of components and systems, advanced manufacturing, large scale adoption of demonstration projects, and energy management with cybersecurity need to be pursued in parallel. Usage and application of H2 based technologies will be reviewed in Part III of the H2 Economy review series in decarbonizing various markets.

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