

HYDROGEN STORAGE

Kunihiro Takahashi

Tokyo Gas Co., Ltd., Japan

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Summary

This topic introduces hydrogen storage. There are various hydrogen storage methods including storage in the gaseous state, storing as a liquid, and storage as a compound or in combination with another medium. The method of storing hydrogen in the gaseous

state is most generally used, and employs tanks or storage tanks (at atmospheric pressure or high pressure). In special cases, hydrogen can be stored underground as well. The tanks used are generally made of steel, although tanks produced mainly of fiber-reinforced plastics to reduce the weight have recently appeared on the market. Storing hydrogen in liquid form is done mainly for space rocket use. Here, consideration is given to the refining of raw-material hydrogen, ortho–para conversion, liquefaction process, and insulated storage tanks. Reference is also made to slush hydrogen. Hydrogen storage using compounds and metal hydrides, which has been put to practical use to a limited extent, is introduced along with an explanation of the new technological developments of metal hydrides. The subject of hydrogen storage using organic compounds mainly discusses ammonia, methanol, and methylcyclohexane. Technology for these compounds as chemical products has already been established, but from the viewpoint of storing and transporting hydrogen, the method of using organic compounds for the storage and short-distance transportation of small quantities of hydrogen is not economical. Therefore, the ongoing research into the feasibility of a hydrogen storage method using the system of hydrogen production and marine transportation relying on renewable energy is also discussed. The system mentioned here is considered as a global-scale energy utilization system. There are methods of storing hydrogen combined with other media such as carbon materials including activated carbon and carbon nanotubes, as well as glass microspheres and zeolite. However, research and development of these methods has begun only recently. The practicability of these methods depends very much on the future research.

1. Introduction

Very little hydrogen exists in nature in the form of H_2 , and so it is not suitable as a primary energy resource. Nevertheless, some 500 billion m^3N is produced worldwide, by all processing methods from fossil fuels or water resources, as described in the Topics *Hydrogen Production from Fossil Fuels*, *Hydrogen Production from Water* and *Innovative Hydrogen Production from Water*.

The hydrogen that is produced can be utilized as either an energy carrier or a chemical material. Hydrogen storage referred to here is related closely to production and utilization (consumption) as well as transportation. The normal flow from production to utilization of hydrogen is summarized as follows:

Production → Storage → Transportation → Storage → Utilization

In fact, however, intermediate steps may be omitted, depending on the proximity between the location of production and that of end consumption and on the pattern of utilization.

Methods of storing hydrogen can be divided roughly into the following three categories:

1. Storage as gas under normal pressure or compressed. The vessel used for storage is a cylinder, tank or, in special cases, the earth's crust (e.g., an abandoned mine). These storage methods are used most.
2. Storage as liquid at super-cold temperature. Hydrogen is stored in a special insulated vessel.

3. Storage as a compound or united with a medium (adsorbent or the like). Such compounds include metal hydride as an inorganic compound, and methanol, ammonia, methylcyclohexane, and others as organic compounds. Typical adsorption mediums are activated carbon, zeolite, and graphite nanofiber.

Methods	Gaseous		Liquid hydrogen	Underground storage	Metal hydride	Activated carbon adsorption
	Normal pressure	Pressurized				
Content	Wet or dry type storage Larger capacity feasible Normally, the capacity is up to about 3000 m ³ for wet storage of hydrogen.	High pressure & ordinary temperature Pressure tank: 1–3 MPa –25000 m ³ N Gas cylinders, etc.: 15–20 MPa –2800 m ³ N (Ref.: Some vessels for city gas are of 200 000 m ³ capacity.)	Atmospheric pressure, 20.4 K 70.8 kg m ⁻³ Insulated vessel (Dewar or tank) Max. 3200 m ³	High pressure & atmospheric temperature Press hydrogen into an abandoned mine, a rock-salt layer, or an aquifer. 10 ⁶ –10 ⁹ m ³ N This method has been put into practice.	At or about atmospheric temperature and pressure Production of metal hydride Contraction to 1000 ⁻¹ Reaction in heat exchange formula Storage in vessel This method has been put into practice.	Low temperature & High pressure 70–220 K 5–10 MPa Combined use of physical adsorption and compressive packing Under R&D scheme
Merits	Relatively easy handling of gaseous hydrogen because of low pressure	Ordinary technical skill Low energy consumption (storage)	High compressive density High bulk density Large storage capacity	Inexpensive Suitable for large storage Good for long-term storage	Greater safety Large volume density Discharge by heat	Density is higher as compared with pressurized gas. Light weight and cheap price
Demerits	Rather poor efficiency of storage (H ₂ wt/total wt)	High pressure Low packing density Better suited for small- or medium-size storage vessels	Large power requirement and high cost of liquefaction Boil-off Flashing	Limited availability of sites	Expensive alloy material Need of initial activation Finely powdered with poison	This method requires liquid nitrogen or other coolants. Vessels used in this method must have sufficient pressure tightness. Selective adsorbency

Table 1. Comparison of hydrogen storage methods.

Regardless of the storage method used, a containment vessel is required. The characteristics of the major storage methods are shown in Table 1 and the packing density of hydrogen in Figure 1.

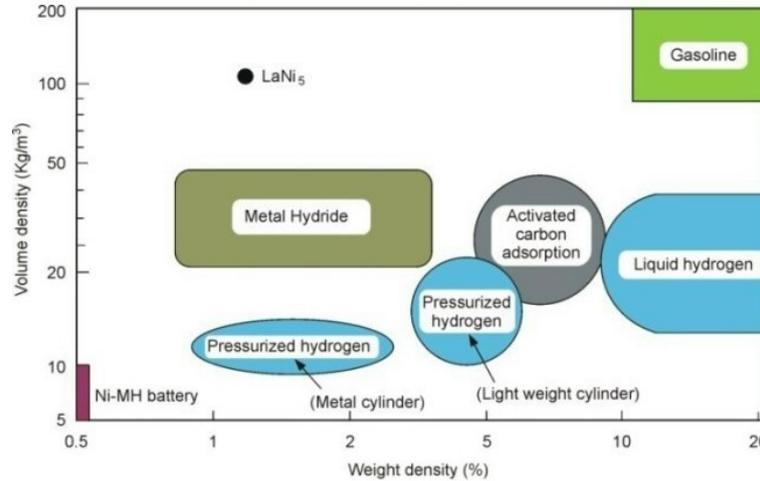


Figure 1. Comparison of hydrogen packing densities (inclusive of vessels). In the case of gasoline and nickel hydride (Ni-MH) battery, Energy density should be converted to hydrogen density.

2. Gas Storage in a Gaseous State

2.1 Storage under Atmospheric Pressure

Usually, gas is stored in a water-sealed gas holder or a dry-type gas holder. In either case, the storage pressure can be maintained at around several thousand pascals.

2.1.1 Water-sealed Gas Holder

The water-sealed type gas holder is shown schematically in Figure 2 and the sealing mechanism in Figure 3.

Storage quantity changes when the level of the gas container rises or falls. Pressure also changes depending on the number of gas containers.

Because of the large weight of sealing water, a large capacity holder tends to be more solid and to have larger volume, so the storage efficiency (hydrogen weight/holder weight) is slightly lower. The available capacity should be around 3000 m³ at maximum. Though the gas may be handled with relative ease, the sealing water must be controlled very carefully. The total number of holder units in service tends to decrease with time.

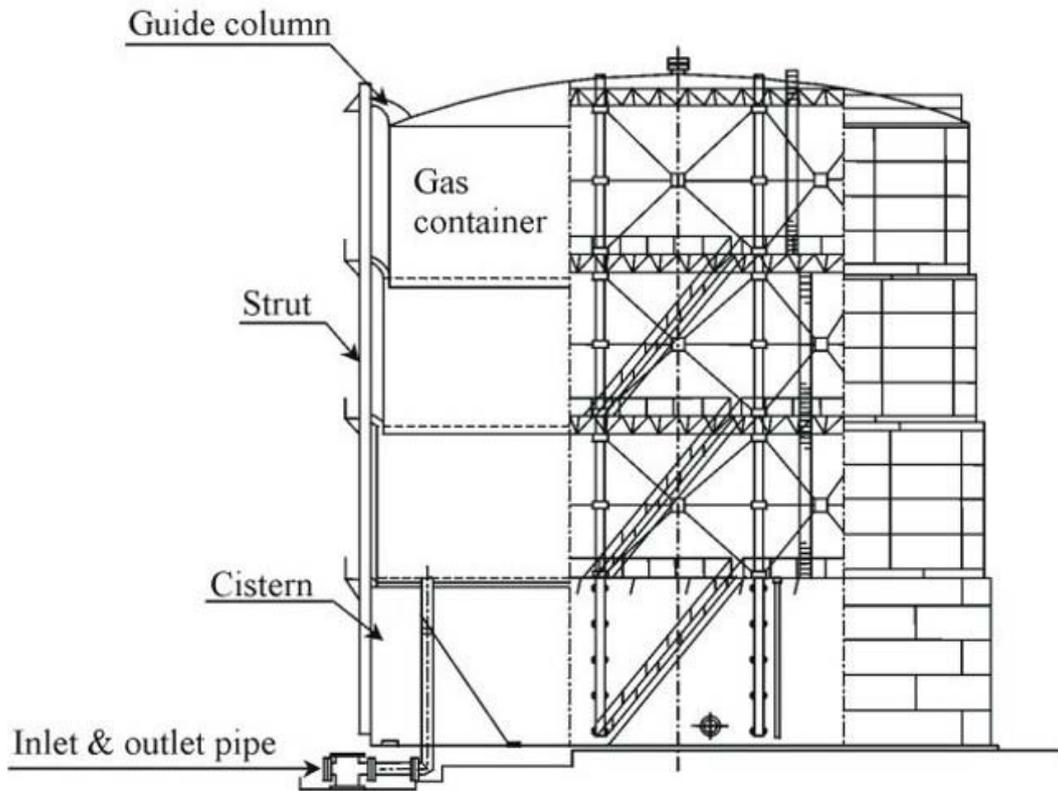


Figure 2. An example of water-sealed gas holder.

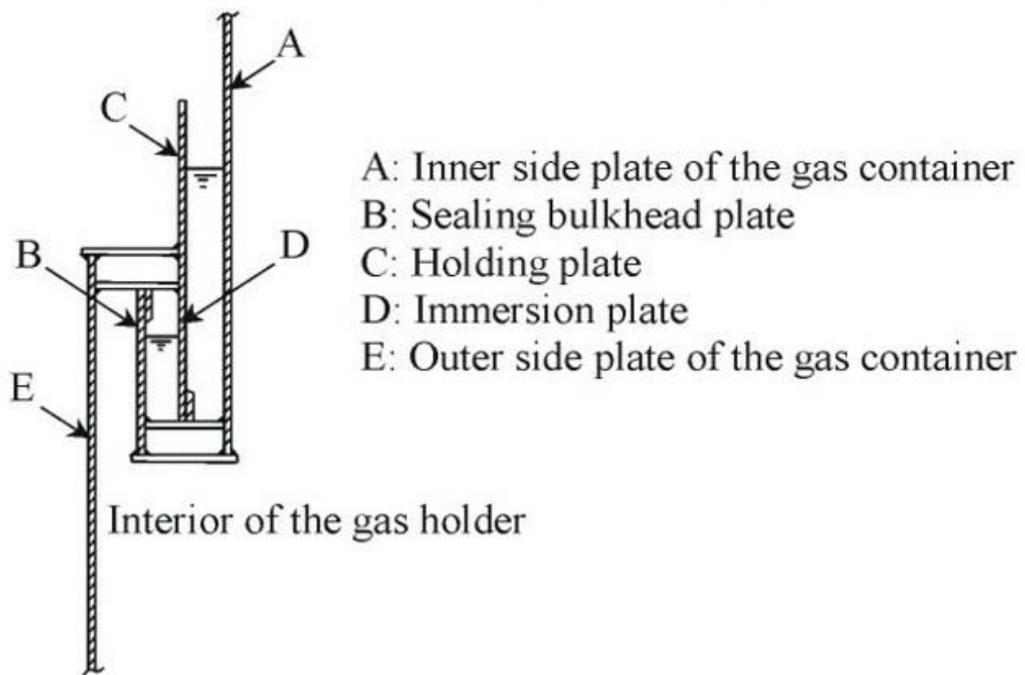


Figure 3. Structure of gas sealing bulkhead.

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Bibliography

Amankwah K.A.G., Noh J.S., Shwarz J.A. (1989). Hydrogen storage on superactivated carbon at refrigeration temperature. *International Journal of Hydrogen Energy* **14**, 437–447. [Study comparing the economy of pressurized hydrogen, liquid hydrogen, metal hydride, and improved activated carbon as hydrogen storage systems.]

Avery W. H., Richard D., and Dugger G. L. (1985). Hydrogen generation by OTEC electrolysis, and economical energy transfer to world markets via ammonia and methanol. *International Journal of Hydrogen Energy* **10**, 727–736. [Evaluation of cases of ammonia and methanol use for storage and transportation of hydrogen in the ocean thermal energy conversion system, which produces hydrogen by electrolysis of water using solar batteries in tropical sea areas.]

Carpentis C. (1988). Storage, transport and distribution of hydrogen. *Hydrogen as an Energy Carrier—Technologies, Systems, Economy* (ed. C.-J. Winter and J. Nitsch), pp. 249–289. [Explanation and evaluation of several systems for storage and transportation of hydrogen.]

Chambers A., Park C., Baker R.T.K., Rodriguez N.M (1998). Hydrogen storage in graphite nanofibers. *Journal of Physical Chemistry* **102**, 4253–4526. [Graphite nanofibers have an extremely high hydrogen adsorbing capacity, confirmed experimentally; an attempt to explain this relative to their distinctive structure.]

Dillon A. C. (1997). Storage of hydrogen in single-walled carbon nanotube. *Nature* **386**, 377–379. [Experiment done to determine the reason for the high hydrogen adsorbing capacity of carbon nanotubes; mentions that hydrogen gas is very densely condensed by the capillary phenomenon.]

Duret B. and Sandin A. (1994). Microspheres for on-board hydrogen storage. *International Journal of Hydrogen Energy* **19**, 757–764. [Theoretical consideration of the case of hydrogen-filled microspheres, and confirmation of hydrogen adsorbing capacity by laboratory-scale experiment.]

Fukuda K. (1999). Generalization of WE-NET first-term research and development results. *WE-NET Hydrogen Energy Symposium (Proceedings)*, pp. 1–26. [Generalized report on WE-NET first-term research and development results concerning the global-scale energy utilization plan which Japan is studying, involving the combination of hydrogen and renewable energy (in Japanese).]

Gürsu S., Sheriff S. A., Veziroglu T. N., and Sheffield J. W. (1994). Review of slush hydrogen production and utilization technologies. *International Journal of Hydrogen Energy* **19**, 491–496. [Review concerning methods of producing and utilizing slush hydrogen in which liquid hydrogen, solid hydrogen, and gaseous hydrogen are in a state of equilibrium.]

Gutmann F. and Murphy O. J. (1983). *The Electrochemical Splitting of Water: Modern Aspects of Electrochemistry No. 15* (ed. R. E. White, J. O'M. Bockris, and B. E. Conway), pp. 1–82. Plenum press. [General explanation, from production to storage of hydrogen.]

Hanada T. (1978). Present situation and future of liquid hydrogen. *High Pressure Gas* **15**(6), 18–33. [General description of circumstances of liquid hydrogen (in Japanese).]

Huston E. L. (1984). Liquid and solid storage of hydrogen. *Hydrogen Energy Progress* **3**, 1171–1186. [Discusses hydrogen storage methods, both liquid-phase such as liquid hydrogen and ammonia, etc., and solid-phase such as metal hydride and zeolite, etc., and compares their economy.]

Jensen C. M., Zidan R., Mariels N., Hee A., and Hagen C. (1999). Advanced titanium doping of sodium aluminum hydride: Segue to a practical hydrogen storage material? *International Journal of Hydrogen Energy* **24**, 461–465. [Explains the effects for processing of NaAlH₄ by titanium.]

Kramer H., Levy M., and Warshawsky A. (1995). Hydrogen storage by the bicarbonate/formate reaction studies on the activity of Pd catalysts. *International Journal of Hydrogen Energy* **20**, 229–233. [Study of activity of palladium (Pd) system catalyst in the bicarbonate/formate system hydrogen storage method.]

Maria G., Marin A., Wyss C., Muller S., and Newson E. (1996). Modelling and scaleup of the kinetics with deactivation of methylcyclohexane dehydrogenation for hydrogen energy storage. *Chemical Engineering Science* **51**, 2891–2896. [Explains relationships between reaction conditions and catalyst activity, and degradation of catalyst, concerning storage of hydrogen by the methylcyclohexene–toluene system.]

Ohsumi Y. (1995). Storage and transportation of hydrogen using metal hydride. *Most Advanced Hydrogen Energy Technology* (ed. T. Ohta), pp. 208–254. Tokyo, Japan, NTS Publishing Co., Ltd. [Explains characteristics of metal hydride and storage and transportation of hydrogen by metal hydrides (in Japanese).]

Seifritz W. (1989). Methanol as the energy vector of a new climate-neutral energy system. *International Journal of Hydrogen Energy* **14**, 717–726. [Study of production of carbon source from fossil fuel for storage of hydrogen by methanol system, and hydrogen-production method with consideration of utilization of high-temperature gas cooled reactor for nuclear power generation.]

Sherif S. A., Zeytinoglu N., and Veziroglu T. N. (1997). Liquid hydrogen: potential, problems, and a proposed research program. *International Journal of Hydrogen Energy* **22**, 683–688. [Study of cost, stability, convenience, and energy density characteristics of hydrogen storage methods, compares gas, liquid, slush and solid (metal hydride) hydrogen storage methods.]

Uehara I. (1998). Production, storage, transportation and utilization of hydrogen. *Metal Hydrides* (ed. H. Tamura), pp. 8–29. Tokyo, Japan, NTS Publishing Co., Ltd. [General information on storage and transportation of hydrogen: the introduction to the above mentioned book describing Metal hydrides (in Japanese).]

Venter R. D. and Pucher G. (1997). Modelling of stationary bulk hydrogen storage systems. *International Journal of Hydrogen Energy* **22**, 791–798. [Investigation of mined salt caverns, depleted natural gas reservoirs and liquid storage vessels, concerning stationary bulk hydrogen storage reservoir system.]

Weit Kamp J., Frits M., and Ernst S. (1995). Zeolite as media for hydrogen storage. *International Journal of Hydrogen Energy* **20**, 967–970. [Comparison and study of the different hydrogen-adsorbing capacities of zeolites with different pore structures and compositions. Zeolites with sodalite cages in their structures were found to have excellent hydrogen-adsorbing capacity.]

Biographical Sketch

Kunihiro Takahashi, born January 28, 1942 in Japan, graduated from the Chemical System Engineering Department, Faculty of Engineering, the University of Tokyo; completed a master course with major in engineering, the University of Tokyo; joined Tokyo Gas Co., Ltd; presently general manager of the Center for Supply Control and Disaster Management, Tokyo Gas Co., Ltd.

Previous positions include: a member of General Research Laboratory of Tokyo Gas Co., Ltd. (1967–1977); general manager of Technical Development Department, general manager of Engineering Department, and general manager of System Energy Department of The Japan Gas Association (1994–

1997). He was appointed as a member of Sub-task-1-committee of WE-NET committee of New Energy and Industrial Technology Development Organization (1994–1997); has held present position since June 1997. Research areas include production processes and catalysts for hydrogen-rich gas and methane-rich gas.

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