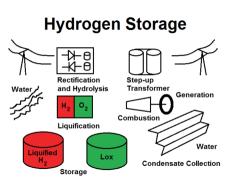
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Hydrogen storage

Hydrogen storage is a term used for any of several methods for storing <u>hydrogen</u> for later use. These methods encompass mechanical approaches such as high pressures and low temperatures, or chemical compounds that release H_2 upon demand. While large amounts of hydrogen is produced, it is mostly consumed at the site of production, notably for the synthesis of <u>ammonia</u>. Interest in hydrogen storage is driven by the idea that it could be a medium for storing energy, e.g. to compensate for <u>intermittent energy</u> <u>sources</u>. The overarching challenge is the very low boiling point of H2: it boils around 20.268 K (-252.882 °C or -423.188 °F). Achieving such low temperatures requires significant energy.



Utility scale underground liquid hydrogen storage

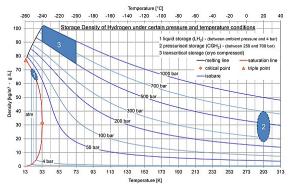
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Established technologies

Compressed and liquefied hydrogen

<u>Compressed hydrogen</u> is a storage form whereby hydrogen gas is kept under pressures to increase the storage density. Compressed hydrogen in hydrogen tanks at 350 bar (5,000 psi) and 700 bar (10,000 psi) is used for hydrogen tank systems in vehicles, based on type IV carbon-composite technology.^[1] Car manufacturers have been developing this solution, such as Honda^[2] or Nissan.^[3]



Net storage density of hydrogen

Liquefied

Liquid hydrogen tanks for cars, producing for example the BMW Hydrogen 7. Japan has a liquid hydrogen (LH2) storage site in Kobe port..^[4] Hydrogen is liquefied by reducing its temperature to -253°C, similar to liquefied natural gas (LNG) which is stored at -162°C. A potential efficiency loss of 12.79% can be achieved, or 4.26kWh/kg out of 33.3kWh/kg.^[5]

Chemical storage

Chemical storage could offer high storage performance due to the high storage densities. For example, supercritical hydrogen at 30 °C and 500 bar only has a density of 15.0 mol/L while methanol has a density of 49.5 mol H_2/L methanol and saturated dimethyl ether at 30 °C and 7 bar has a density of 42.1 mol H_2/L dimethyl ether.

Regeneration of storage material is problematic. A large number of chemical storage systems have been investigated. H2 release can be induced by <u>hydrolysis</u> reactions or catalyzed dehydrogenation reactions. Illustrative storage compounds are hydrocarbons, boron hydrides, <u>ammonia</u>, and <u>alane etc.^[6]</u> A most promising chemical approach is electrochemical hydrogen storage, as the release of hydrogen can be controlled by the applied electricity.^[7] Most of the materials listed below can be directly used for electrochemical hydrogen storage.

The only hydrides capable of achieving the 9 wt% gravimetric goal for 2015 (see chart above) are limited to lithium, boron and aluminium based compounds; at least one of the second-row elements or Al must be added.

As shown before, <u>nanomaterials</u> offer advantage for hydrogen storage systems. Nanomaterials offer an alternative that overcomes the two major barriers of bulk materials, rate of sorption and release temperature.

Enhancement of sorption kinetics and storage capacity can be improved through nanomaterial-based catalyst doping, as shown in the work of the Clean Energy Research Center in the University of South Florida.^[8] This research group studied LiBH₄ doped with <u>nickel</u> nanoparticles and analyzed the weight loss and release temperature of the different species. They observed that an increasing amount of nanocatalyst lowers the release temperature by approximately 20°C and increases the weight loss of the material by 2-3%. The optimum amount of Ni particles was found to be 3 mol%, for which the temperature was within the limits established (around 100°C) and the weight loss was notably greater than the undoped species.

The rate of hydrogen sorption improves at the nanoscale due to the short diffusion distance in comparison to bulk materials. They also have favorable surface-area-to-volume ratio.

The release temperature of a material is defined as the temperature at which the desorption process begins. The energy or temperature to induce release affects the cost of any chemical storage strategy. If the hydrogen is bound too weakly, the pressure needed for regeneration is high, thereby cancelling any energy savings. The target for onboard hydrogen fuel systems is roughly <100 °C for release and <700 bar for recharge (20–60 kJ/mol H₂).^[9]A modified van 't Hoff equation, relates temperature and partial pressure of hydrogen during the desorption process. The modifications to the standard equation are related to size effects at the nanoscale.

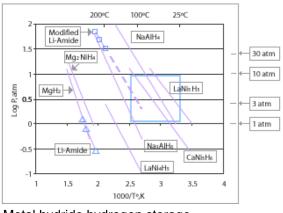
$$ln(p_{
m H_2}) = rac{\Delta H(r)}{RT} + rac{3V_{
m m}\gamma}{rRT} + rac{\Delta S(r)}{R}$$

Where p_{H_2} is the partial pressure of hydrogen, ΔH is the <u>enthalpy</u> of the sorption process (exothermic), ΔS is the change in <u>entropy</u>, R is the ideal <u>gas constant</u>, T is the temperature in Kelvin, V_m is the <u>molar volume</u> of the metal, r is the radius of the nanoparticle and γ is the surface free energy of the particle.

From the above relation we see that the enthalpy and entropy change of desorption processes depend on the radius of the nanoparticle. Moreover, a new term is included that takes into

Metal hydrides

Metal hydrides, such as MgH_2 , $NaAlH_4$, $LiAlH_4$, LiH, $LaNi_5H_6$, $TiFeH_2$, ammonia borane, and palladium hydride represent source of stored hydrogen. Again the persistent problems are the % weight of H2 that they carry and the reversibility of the storage process.^[11] Some are easy-to-fuel liquids at ambient temperature and pressure, whereas others are solids which could be turned into pellets. These materials have good energy density, although their specific energy is often worse than the leading hydrocarbon fuels.



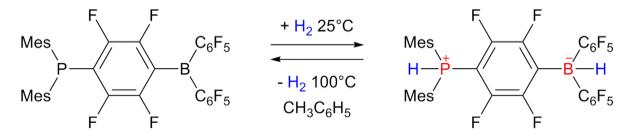
Metal hydride hydrogen storage

LiNH₂, LiBH₄, and NaBH₄.^[12]

An alternative method for lowering dissociation temperatures is doping with activators. This strategy has been used for <u>aluminium hydride</u>, but the complex synthesis makes the approach unattractive.^[13]

Proposed hydrides for use in a hydrogen economy include simple hydrides of magnesium^[14] or transition metals and complex metal hydrides, typically containing sodium, lithium, or calcium and aluminium or boron. Hydrides chosen for storage applications provide low reactivity (high safety) and high hydrogen storage densities. Leading candidates are lithium hydride, sodium borohydride, lithium aluminium hydride and ammonia borane. A French company McPhy Energy is developing the first industrial product, based on magnesium hydride, already sold to some major clients such as Iwatani and ENEL.

Reversible hydrogen storage is exhibited by <u>frustrated Lewis pair</u>, which produces a borohydride.^{[15][16][17]}



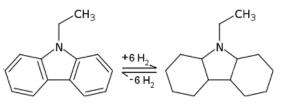
The phosphino-borane on the left accepts one equivalent of hydrogen at one atmosphere and 25 °C and expels it again by heating to 100 °C. The storage capacity is 0.25 wt%.

Aluminium

Hydrogen can be produced using aluminium by reacting it with water.^[18] To react with water, however, aluminium must be stripped of its natural <u>oxide</u> layer, a process which requires pulverization,^[19] chemical reactions with caustic substances, or alloys.^[20] The byproduct of the reaction to create hydrogen is aluminum oxide, which can be recycled back into aluminium with the Hall–Héroult process, making the reaction theoretically renewable. However, this requires electrolysis, which consumes a large amount of energy

Organic hydrogen carriers

Unsaturated organic compounds can store huge amounts of hydrogen. These *Liquid Organic Hydrogen Carriers* (LOHC) are hydrogenated for storage and dehydrogenated again when the energy/hydrogen is needed. Using LOHCs relatively high gravimetric storage densities can be reached (about 6 wt-%) and the overall energy efficiency is higher than for other chemical storage



Reversible hydrogenation of N-ethylcarbazole.

options such as producing methane from the hydrogen.^[21] Both hydrogenation and dehydrogenation of LOHCs requires catalysts.^[22] It was demonstrated that replacing hydrocarbons by hetero-atoms, like N, O etc. improves reversible de/hydrogenation properties.

Cycloalkanes

Research on LOHC was concentrated on cycloalkanes at an early stage, with its relatively high hydrogen capacity (6-8 wt %) and production of CO_x -free hydrogen.^[22] Heterocyclic aromatic compounds (or N-Heterocycles) are also appropriate for this task. A compound featuring in LOHC research is N-Ethylcarbazole (NEC)^[23] but many others do exist.^[24] Dibenzyltoluene (h ttps://pubchem.ncbi.nlm.nih.gov/compound/2_3-Dibenzyltoluene), which is already used as a heat transfer fluid in industry, was identified as potential LOHC. With a wide liquid range between -39 °C (melting point) and 390 °C (boiling point) and a hydrogen storage density of 6.2 wt% dibenzyltoluene is ideally suited as LOHC material.^[25] Formic acid has been suggested as a promising hydrogen storage material with a 4.4wt% hydrogen capacity.^[26]

Cycloalkanes reported as LOHC include cyclohexane, methyl-cyclohexane and decalin. The dehydrogenation of cycloalkanes is highly endothermic (63-69 kJ/mol H₂), which means this process requires high temperature.^[22] Dehydrogenation of decalin is the most thermodynamically favored among the three cycloalkanes, and methyl-cyclohexane is second because of the presence of the methyl group.^[27] Research on catalyst development for dehydrogenation of cycloalkanes has been carried out for decades. Nickel (Ni), Molybdenum (Mo) and Platinum (Pt) based catalysts are highly investigated for dehydrogenation. However, coking is still a big challenge for catalyst's long-term stability.^{[28][29]}

N-Heterocycles

The temperature required for hydrogenation and dehydrogenation drops significantly for heterocycles vs simple carbocycles.^[30] Among all the N-heterocycles, the saturated-

unsaturated pair of dodecahydro-N-ethylcarbazole (12H-NEC) and NEC has been considered as a promising candidate for hydrogen storage with a fairly large hydrogen content (5.8wt%).^[31] The figure on the top right shows dehydrogenation and hydrogenation of the 12H-NEC and NEC pair. The standard catalyst for NEC to 12H-NEC is Ru and Rh based. The selectivity of hydrogenation can reach 97% at 7 MPa and 130 °C-150 °C.^[22] Although N-Heterocyles can optimize the unfavorable thermodynamic properties of cycloalkanes, a lot of issues remain unsolved, such as high cost, high toxicity and kinetic barriers etc.^[22]

The imidazolium ionic liquids such alkyl(aryl)-3-methylimidazolium N-bis(trifluoromethanesulfonyl)imidate salts can reversibly add 6–12 hydrogen atoms in the presence of classical Pd/C or Iro nanoparticle catalysts and can be used as alternative materials for on-board hydrogen-storage devices. These salts can hold up to 30 g L^{-1} of hydrogen at atmospheric pressure.^[32]

Formic acid

Formic acid is a highly effective hydrogen storage material, although its H2 density is low. Carbon monoxide free hydrogen has been generated in a very wide pressure range (1–600 bar). A homogeneous catalytic system based on water-soluble ruthenium catalysts selectively decompose HCOOH into H₂ and CO₂ in aqueous solution.^[33] This catalytic system overcomes the limitations of other catalysts (e.g. poor stability, limited catalytic lifetimes, formation of CO) for the decomposition of formic acid making it a viable hydrogen storage material.^[34] And the co-product of this decomposition, carbon dioxide, can be used as hydrogen vector by hydrogenating it back to formic acid in a second step. The catalytic hydrogenation of CO₂ has long been studied and efficient procedures have been developed.^{[35][36]} Formic acid contains 53 g L⁻¹ hydrogen at room temperature and atmospheric pressure. By weight, pure formic acid stores 4.3 wt% hydrogen. Pure formic acid is a liquid with a flash point 69 °C (cf. gasoline -40 °C, ethanol 13 °C). 85% formic acid is not flammable.

Carbohydrates

<u>Carbohydrates</u> (polymeric $C_6H_{10}O_5$) releases H_2 in a bioreformer mediated by the enzyme cocktail—cell-free synthetic pathway biotransformation. Carbohydrate provides high hydrogen storage densities as a liquid with mild pressurization and cryogenic constraints: It can also be stored as a solid powder. Carbohydrate is the most abundant renewable bioresource in the world.

Ammonia and related compounds

Ammonia

Ammonia (NH_3) releases H_2 in an appropriate catalytic reformer. Ammonia provides high hydrogen storage densities as a liquid with mild pressurization and cryogenic constraints: It can also be stored as a liquid at room temperature and pressure when mixed with water. Ammonia is the second most commonly produced chemical in the world and a large infrastructure for making, transporting, and distributing ammonia exists. Ammonia can be reformed to produce hydrogen with no harmful waste, or can mix with existing fuels and under the right conditions burn efficiently. Since there is no carbon in ammonia, no carbon by-products are produced; thereby making this possibility a "carbon neutral" option for the future. Pure ammonia burns poorly at the atmospheric pressures found in natural gas fired water heaters and stoves. Under compression in an automobile engine it is a suitable fuel for slightly modified gasoline engines. Ammonia is the suitable alternative fuel because it has 18.6 MJ/kg energy density at NTP and carbon-free combustion byproducts.^[37] However, ammonia is a toxic gas at normal temperature and pressure and has a potent odor.^[38] Hydrogen can be separated from unreacted ammonia using a membrane technology. ^[39]

In September 2005 chemists from the Technical University of Denmark announced a method of storing hydrogen in the form of ammonia saturated into a salt tablet. They claim it will be an inexpensive and safe storage method.^[40]

Hydrazine

Hydrazine breaks down in the cell to form nitrogen and hydrogen/^[41] Silicon hydrides and germanium hydrides are also candidates of hydrogen storage materials, as they can subject to energetically favored reaction to form covalently bonded dimers with loss of a hydrogen molecule.^{[42] [43]}

Amine boranes

Prior to 1980, several compounds were investigated for hydrogen storage including complex borohydrides, or aluminohydrides, and ammonium salts. These hydrides have an upper theoretical hydrogen yield limited to about 8.5% by weight. Amongst the compounds that contain only B, N, and H (both positive and negative ions), representative examples include: amine boranes, boron hydride ammoniates, hydrazine-borane complexes, and ammonium octahydrotriborates or tetrahydroborates. Of these, amine boranes (and especially ammonia borane) have been extensively investigated as hydrogen carriers. During the 1970s and 1980s, the U.S. Army and Navy funded efforts aimed at developing hydrogen/deuterium gas-generating compounds for use in the HF/DF and HCl chemical lasers, and gas dynamic lasers. Earlier hydrogen gas-generating formulations used amine boranes and their derivatives. Ignition of the amine borane(s) forms boron nitride (BN) and hydrogen gas. In addition to ammonia borane (H₃BNH₃), other gas-generators include diborane diammoniate, H₂B(NH₃)₂BH₄.

Physical storage

In this case hydrogen remains in physical forms, i.e., as gas, supercritical fluid, adsorbate, or molecular inclusions. Theoretical limitations and experimental results are considered ^[44] concerning the volumetric and gravimetric capacity of glass microvessels, microporous, and nanoporous media, as well as safety and refilling-time demands.

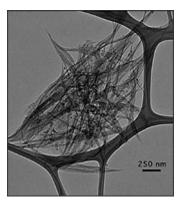
Porous or layered carbon

Activated carbons are highly porous amorphous carbon materials with high apparent surface area. Hydrogen <u>physisorption</u> can be increased in these materials by increasing the apparent surface area and optimizing pore diameter to around 7 Å.^[45] These materials are of particular interest due to the fact that they can be made from waste materials, such as cigarette butts which have shown great potential as precursor materials for high-capacity hydrogen storage materials.^{[46][47]}

<u>Graphene</u> can store hydrogen efficiently. The H_2 adds to the double bonds giving graphane. The hydrogen is released upon heating to 450 °C.^{[48][49]}

Hydrogen carriers based on nanostructured carbon (such as carbon <u>buckyballs</u> and <u>nanotubes</u>) have been proposed. However, hydrogen content amounts up to ~3.0-7.0 wt% at 77K which is far from the value set by US Department of Energy (6 wt% at nearly ambient conditions).

To realize carbon materials as effective hydrogen storage technologies, carbon nanotubes (CNTs) have been doped with MgH_2 .^[8] The metal hydride has proven to have a theoretical storage capacity (7.6 wt%) that fulfills the United States Department of Energy requirement of 6 wt%, but has limited practical applications due to its high release temperature. The proposed mechanism involves the creation of fast diffusion channels by CNTs within the MgH₂ lattice. Fullerene is other



Carbon nanotubes

carbonaceous nanomaterials that has been tested for hydrogen storage in this center. Fullerene molecules are composed of a C_{60} close-caged structure, that allows for hydrogenation of the double bonded carbons leading to a theoretical $C_{60}H_{60}$ isomer with a hydrogen content of 7.7 wt%. However, the release temperature in these systems is high (600°C).

Metal-organic frameworks

<u>Metal-organic frameworks</u> represent another class of synthetic porous materials that store hydrogen and energy at the molecular level. MOFs are highly crystalline inorganic-organic hybrid structures that contain metal clusters or ions (secondary building units) as nodes and organic ligands as linkers. When guest molecules (solvent) occupying the pores are removed during solvent exchange and heating under vacuum, porous structure of MOFs can be achieved without destabilizing the frame and hydrogen molecules will be adsorbed onto the surface of the pores by physisorption. Compared to traditional zeolites and porous carbon materials, MOFs have very high number of pores and surface area which allow higher hydrogen uptake in a given volume. Thus, research interests on hydrogen storage in MOFs have been growing since 2003 when the first MOF-based hydrogen storage was introduced. Since there are infinite geometric and chemical variations of MOFs based on different combinations of SBUs and linkers, many researches explore what combination will provide the maximum hydrogen uptake by varying materials of metal ions and linkers. In 2006, chemists at UCLA and the University of Michigan have achieved hydrogen storage concentrations of up to 7.5 wt% in MOF-74 at a low temperature of 77 K.^{[50][51]} In 2009, researchers at University of Nottingham reached 10 wt% at 77 bar (1,117 psi) and 77 K with MOF NOTT-112.^[52] Most articles about hydrogen storage in MOFs report hydrogen uptake capacity at a temperature of 77K and a pressure of 1 bar because these conditions are commonly available and the binding energy between hydrogen and the MOF at this temperature is large compared to the thermal vibration energy. Varying several factors such as surface area, pore size, catenation, ligand structure, and sample purity can result in different amounts of hydrogen uptake in MOFs.

In 2020, researchers at Northwestern University in the USA reported that NU-1501-Al, an ultraporous metal–organic framework (MOF) based on metal trinuclear clusters, yielded "impressive gravimetric and volumetric storage performances for hydrogen and methane", with a hydrogen delivery capacity of 14.0% w/w, 46.2 g/litre. ^[53] ^[54]

Cryo-compressed

Cryo-compressed storage of hydrogen is the only technology that meets 2015 DOE targets for volumetric and gravimetric efficiency (see "CcH2" on slide 6 in ^[55]).

Furthermore, another study has shown that cryo-compressed exhibits interesting cost advantages: ownership cost (price per mile) and storage system cost (price per vehicle) are actually the lowest when compared to any other technology (see third row in slide 13 of ^[56]). For example, a cryo-compressed hydrogen system would cost \$0.12 per mile (including cost of fuel and every associated other cost), while conventional gasoline vehicles cost between \$0.05 and \$0.07 per mile.

Like liquid storage, cryo-compressed uses cold hydrogen (20.3 K and slightly above) in order to reach a high energy density. However, the main difference is that, when the hydrogen would warm-up due to heat transfer with the environment ("boil off"), the tank is allowed to go to pressures much higher (up to 350 bars versus a couple of bars for liquid storage). As a consequence, it takes more time before the hydrogen has to vent, and in most driving situations, enough hydrogen is used by the car to keep the pressure well below the venting limit.

Consequently, it has been demonstrated that a high driving range could be achieved with a cryo-compressed tank : more than 650 miles (1,050 km) were driven with a full tank mounted on an hydrogen-fueled engine of Toyota Prius.^[57] Research is still underway to study and demonstrate the full potential of the technology.^[58]

As of 2010, the BMW Group has started a thorough component and system level validation of cryo-compressed vehicle storage on its way to a commercial product.^[59]

Clathrate hydrates

 $\underline{H_2 \text{ caged}}$ in a <u>clathrate hydrate</u> was first reported in 2002, but requires very high pressures to be stable. In 2004, researchers from Delft University of Technology and Colorado School of

Glass capillary arrays

A team of Russian, Israeli and German scientists have collaboratively developed an innovative technology based on glass capillary arrays for the safe infusion, storage and controlled release of hydrogen in mobile applications.^{[61][62]} The C.En technology has achieved the United States Department of Energy (DOE) 2010 targets for on-board hydrogen storage systems.^[63] DOE 2015 targets can be achieved using flexible glass capillaries and cryo-compressed method of hydrogen storage.^[64]

Glass microspheres

Hollow glass microspheres (HGM) can be utilized for controlled storage and release of hydrogen. [65][66]

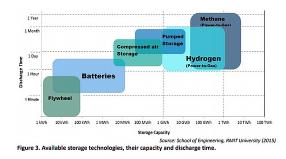
Stationary hydrogen storage

Unlike mobile applications, hydrogen density is not a huge problem for stationary applications. As for mobile applications, stationary applications can use established technology:

- Compressed hydrogen (CGH₂) in a hydrogen tank^[67]
- Liquid hydrogen in a (LH₂) cryogenic hydrogen tank
- Slush hydrogen in a cryogenic hydrogen tank

Underground hydrogen storage

Underground hydrogen storage is the practice of hydrogen storage in <u>caverns</u>, <u>salt domes</u> and depleted oil and gas fields. Large quantities of gaseous hydrogen have been stored in caverns by <u>ICI</u> for many years without any difficulties.^[69] The storage of large quantities of liquid hydrogen underground can function as grid energy storage. The round-trip efficiency is approximately 40% (vs. 75-80% for pumped-hydro (PHES)), and the cost is slightly higher than pumped hydro, if only a limited number of hours of storage is required.^[70] Another study referenced by a European staff



'Available storage technologies, their capacity and discharge time.^{1[68]:12}

working paper found that for large scale storage, the cheapest option is hydrogen at \pounds_{140} /MWh for 2,000 hours of storage using an electrolyser, salt cavern storage and combined-cycle power plant.^{[68]:15} The European project Hyunder^[71] indicated in 2013 that for the

storage of wind and solar energy an additional 85 caverns are required as it cannot be covered by PHES and <u>CAES</u> systems.^[72] A German case study on storage of hydrogen in salt caverns found that if the German power surplus (7% of total variable renewable generation by 2025 and 20% by 2050) would be converted to hydrogen and stored underground, these quantities would require some 15 caverns of 500,000 cubic metres each by 2025 and some 60 caverns by 2050 – corresponding to approximately one third of the number of gas caverns currently operated in Germany.^[73] In the US, Sandia Labs are conducting research into the storage of hydrogen in depleted oil and gas fields, which could easily absorb large amounts of renewably produced hydrogen as there are some 2.7 million depleted wells in existence.^[74]

Power to gas

Power to gas is a technology which converts electrical power to a gas fuel. There are two methods: the first is to use the electricity for water splitting and inject the resulting hydrogen into the natural gas grid; the second, less efficient method is used to convert carbon dioxide and hydrogen to methane, (see natural gas) using electrolysis and the Sabatier reaction. A third option is to combine the hydrogen via electrolysis with a source of carbon (either carbon dioxide or carbon monoxide from biogas, from industrial processes or via direct air-captured carbon dioxide) via biomethanation,^{[75][76]} where biomethanogens (archaea) consume carbon dioxide and hydrogen and produce methane within an anaerobic environment. This process is highly efficient, as the archaea are self-replicating and only require low-grade (60°C) heat to perform the reaction.

Another process has also been achieved by <u>SoCalGas</u> to convert the carbon dioxide in raw biogas to methane in a single electrochemical step, representing a simpler method of converting excess renewable electricity into storable natural gas.^[77]

The UK has completed surveys and is preparing to start injecting hydrogen into the gas grid as the grid previously carried 'town gas' which is a 50% hydrogen-methane gas formed from coal. Auditors KPMG found that converting the UK to hydrogen gas could be £150bn to £200bn cheaper than rewiring British homes to use electric heating powered by lower-carbon sources.^[78]

Excess power or off peak power generated by wind generators or solar arrays can then be used for load balancing in the energy grid. Using the existing natural gas system for hydrogen, Fuel cell maker Hydrogenics and natural gas distributor Enbridge have teamed up to develop such a power to gas system in Canada.^[79]

Pipeline storage of hydrogen where a natural gas network is used for the storage of hydrogen. Before switching to <u>natural gas</u>, the German gas networks were operated using <u>towngas</u>, which for the most part (60-65%) consisted of hydrogen. The storage capacity of the German natural gas network is more than 200,000 GW·h which is enough for several months of energy requirement. By comparison, the capacity of all German pumped storage power plants amounts to only about 40 GW·h. The transport of energy through a gas network is done with much less loss (<0.1%) than in a power network (8%). The use of the existing <u>natural gas</u> pipelines for hydrogen was studied by NaturalHy^[80]

Storage Parameter	2005		2010		2015	
Gravimetric Capacity (Specific energy)	1.5 kWh/kg 0.045 kg H ₂ /kg		2.0 kWh/kg 0.060 kg H ₂ /kg		3.0 kWh/kg 0.090 kg H ₂ /kg	
System Weight:		111 Kg		83 Kg		55.6 Kg
Volumetric Capacity (Energy density)	1.2 kWh/L 0.036 kg H ₂ /L		1.5 kWh/L 0.045 kg H ₂ /L		2.7 kWh/L 0.081 kg H ₂ /L	
System Volume:		139 L		111 L		62 L
Storage system cost	\$6 /kWh	7	\$4 /kWh	7	\$2 /kWh	7
System Cost:		\$1000		\$666		\$333
Refueling rate	.5 Kg H ₂ /min		1.5 Kg H ₂ /min		2.0 Kg H ₂ /min	
Refueling Time:		10 min		3.3 min		2.5 min

Automotive Onboard hydrogen storage

Targets for on-board hydrogen storage assuming storage of 5 kg of hydrogen.^[81]

Targets were set by the FreedomCAR Partnership in January 2002 between the United States Council for Automotive Research (USCAR) and U.S. DOE (Targets assume a 5-kg H₂ storage system). The 2005 targets were not reached in 2005.^[82] The targets were revised in 2009 to reflect new data on system efficiencies obtained from fleets of test cars.^[83] The ultimate goal for volumetric storage is still above the theoretical density of liquid hydrogen.^[84]

It is important to note that these targets are for the hydrogen storage system, not the hydrogen storage material. System densities are often around half those of the working material, thus while a material may store 6 $\underline{\text{wt\%}}$ H₂, a working system using that material may only achieve 3 wt% when the weight of tanks, temperature and pressure control equipment, etc., is considered.

In 2010, only two storage technologies were identified as having the potential to meet DOE targets: MOF-177 exceeds 2010 target for volumetric capacity, while cryo-compressed H_2 exceeds more restrictive 2015 targets for both gravimetric and volumetric capacity (see slide 6 in ^[55]).

The existing options for hydrogen storage require large storage volumes which makes them impractical for stationary and portable applications. Portability is one of the biggest challenges in the <u>automotive industry</u>, where high density storage systems are problematic due to safety concerns.

<u>Fuel cell powered vehicles</u> are required to provide a driving range over 300 miles—this cannot be achieved with traditional storage methods. A long term goal set by the Fuel Cell Technology Office involves the usage of nanomaterials to improve maximum range.^[85]

U.S. Department of Energy's requirements

The Department of Energy has set the targets for onboard hydrogen storage for light vehicles.

The list of requirements include parameters related to gravimetric and volumetric capacity, operability, durability and cost. These targets have been set as the goal for a multiyear research plan expected to offer an alternative to fossil fuels.^[86]

Fuel cells and storage

Due to its clean-burning characteristics, hydrogen is one of the most promising fuel alternatives in the automotive industry. Hydrogen based fuel could significantly reduce the emissions of greenhouse gases such as CO_2 , SO_2 and NO_x . The three limiting factor for the use of hydrogen fuel cells (HFC) include efficiency, size, and safe onboard storage of the gas. Other major disadvantages of this emerging technology involve cost, operability and durability issues, that are still to be improved from the existing systems. To address these challenges, the use of nanomaterials has been proposed as an alternative option to the traditional hydrogen storage systems. The use of nanomaterials could provide a higher density system that is expected to increase the driving range limit set by the <u>DOE</u> at 300 miles. Carbonaceous materials such as <u>CNTs</u> and metal hydrides are the main focus of researchers. Carbonaceous materials are currently being considered for onboard storage systems due to their versatility, multifunctionality, mechanical properties and low cost with respect to other alternatives.^[87]

Other advantages of nanomaterials in fuel cells

The introduction of nanomaterials in onboard hydrogen storage systems can be a major turning point in the automotive industry. However, storing is not the only practical aspect of the fuel cell to which nanomaterials may contribute. Different studies have shown that the transport and catalytic properties of Nafion membranes used in HFCs can be enhanced with TiO_2/SnO_2 nanoparticles.^[87] The increased performance is caused by an improvement in hydrogen splitting kinetics due to catalytic activity of the nanoparticles. Furthermore, this system exhibits faster transport of protons across the cell which makes HFCs with nanoparticle composite membranes a promising alternative.

Another application of nanomaterials in water splitting has been introduced by a research group at <u>Manchester Metropolitan University</u> in the UK using screen-printed <u>electrodes</u> consisting of a <u>graphene-like material.^[88]</u> Similar systems have been developed using photoelectrochemical techniques.

See also

- Cascade storage system
- Cryo-adsorption
- Electrochemical hydrogen compressor
- Hydrogenography
- Hydrogen energy plant in Denmark
- Industrial gas
- Tunable nanoporous carbon

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External links

- MaHyTec Hydrogen Tanks (http://www.mahytec.com/)
- EU Storhy (http://www.storhy.net/)
- Nesshy (http://www.nesshy.net/)
- Vodik (http://www.vodiklabs.com/)
- Hydrogen as the fuel of the future, report by the DLR; discusses the types of hydrogen storage (http://www.dlr.de/fk/en/Portaldata/40/Resources/dokumente/publikationen/Hydrog en_Brinner_2001.pdf)
- United States Department of Energy Planned program activities for 2003–2010 (https://ww w1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/storage.pdf)
- Ammonia Borane (NhxBHx) (https://web.archive.org/web/20080917223841/http://www.pnl. gov/microproducts/conferences/2004/presentations/autrey.pdf)
- Hyweb (1996) (http://www.hyweb.de/Knowledge/w-i-energiew-eng4.html)
- Research into metal-organic framework or Nano Cages [1] (https://www.nist.gov/public_affa irs/techbeat/tb2005_120105.htm#cages)H2 Storage Projects (http://www.ncnr.nist.gov/staff /taner/h2/)
- Hydrogen Storage Technical Data (http://public.ca.sandia.gov/hydrogen/research/storage/i ndex.html)

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