

Storage of liquid hydrogen in natural zeolite

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When producing and utilizing hydrogen, its storage is one of the biggest problems. Hydrogen, as a gas, is extremely fluid with very low specific weight. Moreover, at a certain rate, the hydrogen-oxygen mixture is explosive. Therefore, the storage of hydrogen is relatively dangerous. A storage of liquid hydrogen in the natural zeolite, which is placed in large capacity battery, appears to be a suitable hydrogen storage method. Proposed and constructed pressure tank, large capacity battery, allows long-term and safe storage of liquid hydrogen, with the possibility to change its state from liquid to gaseous or contrarily in real time. Natural zeolite is an inert material with large internal surface area and high thermal capacity. In the future, presented large capacity battery VAZEP can be a part of the system for production and storage of electric energy generated by photovoltaic modules from the sun.

Key words: Liquid hydrogen, natural zeolite, storage, large capacity battery, VAZEP

Introduction

The use of hydrogen as an energy source is one of the real possibilities of non-carbon technologies utilization, as there is only one waste product – vapor – produced by the hydrogen combustion. Utilization of hydrogen includes various possibilities (Farndon, 2000). Gaseous hydrogen, standardly stored and transported in a red stripe labeled pressure tanks, is used for:

- production of chemicals (ammonia, nitric acid, methylene, different kinds of nitrogenous fertilizers);
- production of metals (by reduction of metal oxides);
- solidification of fats (in the food industry);
- desulfurization of petroleum;
- welding and cutting of metals (using oxygen-hydrogen flame);
- protection atmosphere at firing powder metallurgy blanks (a mixture of hydrogen and nitrogen).

Liquid hydrogen is used:

- as a rocket fuel,
- in vehicles with internal combustion engines.

Simplistically, it can be said that, in vehicles with internal combustion engines, the only change is the replacement of gasoline or diesel for hydrogen. Other parts are functionally the same. High distribution costs and unsolved safe long term storage of liquid hydrogen and its tanking at filling stations inhibit from the expansion of hydrogen use in automobile transport.

An important feature of the development of such vehicles is their safety. Although, hydrogen is “safer” than natural gas in open space, as it immediately dissipated and rises in height, its use in enclosed spaces (e.g. vehicles or garages) is dangerous due to its explosive character. Therefore, safety measures are necessary to store hydrogen. It is also connected to the fact that the ignition of hydrogen requires less energy than natural gas ignition (NREL, 2009).

Some technical devices based on hydrogen use

H₂O₂ steam generator – on the principle of rock propulsion, the stoichiometric hydrogen-oxygen mixture is produced. Its burning produces the steam. At the same time, water is injected into burning gas. Water immediately transforms into the steam, increasing the device efficiency. Advantages of this device are high cleanliness, short reaction time, regulation possibilities, and small dimensions.

Combustion engine and gas turbine – it is possible to modify them to use hydrogen propulsion. Reached higher temperatures are used for combined production of electricity and heat. Mixed gas propulsion is trouble-

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free with the hydrogen ratio up to 80 %. Only some device modifications are needed using a mixture of hydrogen and natural gas. At present, turbines with clear hydrogen propulsion are also available. However, problems with high temperatures and different hydrodynamic systems may occur. Such turbines with the power of 3-5-10 MW produce electricity.

Fuel cell – uses the hydrogen energy to produce electricity. The process is based on the electrochemical reaction in the cell. The reaction occurs after the penetration of hydrogen into the cell, decomposing into negatively charged electrons and positive hydrogen ion. Electrons and ions are collected by the anode and cathode located on sides of the cell. Normally they are used to be made from gas permeable graphite paper. Besides hydrogen, fuel cells also use compressed oxygen that penetrated from the opposite side of the cell. Both gases pass through small channels in electrodes. In the middle of the cell, a proton membrane (covered by platinum catalyzer) is located, through which hydrogen ions penetrate and connect with oxygen. The catalyzer causes that positive charge is generated on the hydrogen side of the cell and negative on oxygen side, resulting in the production of electric current. The product (waste) of this reaction is water. Loose electrons cannot penetrate back through the membrane and are “forced to pass” via another way – e.g. via the vehicle electric motor.

The use of hydrogen as a repository for buildings and households – use of photovoltaics together with electrolyzer and fuel cell allows absolute decentralization of home’s energetics. Using photovoltaic panels, households can produce own electricity, and unused surplus can be used for the production of storage of hydrogen. Using this hydrogen and fuel cells, it is possible to produce electricity and use it when photovoltaic panels do not produce sufficient quantity of electricity. The batteries run down, but hydrogen can be produced and stored at any time. The produced hydrogen can also be directly tanked to the car.

Hydrogen boiler for heating buildings – combines hydrogen produces from renewable energy sources and atmospheric oxygen. The reaction of these two gases produces heat. The reaction temperature is electronically limited to 300 °C. The heat is transmitted to the junction exchange station to the heating unit.

Production of hydrogen by electrolysis of water

At present, most of produced and distributed hydrogen is obtained from natural gas conversion. Steam reforming, which is based on the fission of hydrocarbons from fossil fuels by water steam, is the most common within thermo-chemical hydrogen production methods.

Industrial technologies of hydrogen production are discussed in the publications of many authors (e.g. Steinberg, Cheng, 1989; Pena et al., 1996; Ueno et al., 1996; Das, Veziroğlu, 2001; Yu et al., 2002; Turner, 2004; Ni et al., 2006; Holladay et al., 2009; Bhandari et al., 2014; Wang et al., 2014, Ma et al., 2015).

The following text is devoted to the production of hydrogen by electrolysis of water, technology of hydrogen storage introduced in this paper is connected to it.

Taking into account environmental issues of thermos chemical hydrogen production-related CO₂, it can be assumed that this method of hydrogen production will extend with increasing ratio of electricity production from the sun energy.

Recently, only 5 % of hydrogen is produced by the electrolysis of water. Electrolysis of water is an electrochemical redox process resulting in the decomposition of water into oxygen and hydrogen due to an electric current being passed through the water (IEA, 2006).

During the electrolysis of water, hydrogen is formed at cathode, according to reaction:



The equivalent amount of oxygen accumulates at anode:



Combining both reactions yields the equation of overall water decomposition. Changes in standard molar enthalpy show that the reaction is endothermic. It means that the arrangement within the system is reduced during the chemical reaction. So, at the electrolytic decomposition of water, it is necessary to supply energy to the system. By solving thermodynamic equations for reversible voltage, we obtain its value – 1,23 V. Below 1,23 V, the electrolysis does not run, and hydrogen does not generate.

Another important voltage value for electrolysis of water running in electrolyzers is the value at which electric current does not heat electrolyte, so the whole electrolyte is used for disintegration of water. The limit value of this voltage is 1,48 V. At more than 1,48 V, a part of the electric current heats the electrolyte, and it is necessary to keep the equilibrium, to remove generated heat from the electrolyte.

From above mentioned, it can be concluded that optimum voltage interval is 1,23 – 1,48 V. This interval determines the number of anode-cathode couples depending on the supply voltage.

To calculate the hydrogen volume produced by the electrolysis of water, first Faraday's law (Strong, 1961) can be used:

$$V_{theoretical} = \frac{R \cdot I \cdot T \cdot t}{F \cdot p \cdot z}, \quad (3)$$

where:

$R = 8,314 \text{ J}/(\text{K} \cdot \text{mol})$,

I is electric current (in amperes),

T is temperature (in kelvins),

t is time (in seconds),

F is Faraday constant ($9,648 \cdot 10^4 \text{ C/mol}$),

p is pressure (in pascals),

z is the valence number of ions of the substance (electrons transferred per ion; 2 for hydrogen).

Calculation results show that to produce 1 m^3 of hydrogen, it is necessary to supply electric energy of 4 to 4,8 kWh, based on the hydrogen generator efficiency.

Use of photovoltaics in hydrogen production

As can be readily appreciated, electric energy produced by photovoltaic systems offers the clearest way of hydrogen production. During the electrolysis, water disintegrated into hydrogen and oxygen by photoelectric cell (a process called "artificial photosynthesis"). Hydrogen is produced on the front, amorphous, silicone surface of catalyzer and oxygen is produced on back, metal, surface.

Significant progress in the field of catalyzers has been made by the construction of PEM electrolyzers, using clear water to produce hydrogen, so-called Fuel Cell System (FCS) generators.

Generators using electrolyte in the form of solid polymer (SPE) producing hydrogen from deionized water seem to be effective also. Hydrogen is accumulated in a pressure tank at 0,4 MPa and oxygen goes to air. The advantage is that the process is very safe.

Hydrogen storage

The possibility of long-term and safe hydrogen storage is a challenge (Züttel, 2003; Zhou, 2005) and is one of the crucial preconditions allowing the use of hydrogen-based technologies. Recently used methods of hydrogen storage are as follows:

- storage of gaseous hydrogen (CGH) (Züttel, 2003),
- storage of liquid hydrogen (LHG) (Peschka, 1987),
- storage of hydrogen in metal hybrid materials (MH) (Sakintuna et al., 2007),
- storage of hydrogen by adsorption in activated carbon (Texier-Mandoki et al., 2004),
- storage of hydrogen in carbon or zeolite – nanotubes (CNTs) (Züttel et al., 2002),
- storage of hydrogen in materials with the metal-organic framework (MOF) (Rowsell, Yaghi, 2005)
- storage of hydrogen in chemical hybrids (Biniwale et al., 2008).

Recently, the CNTs method (using nanomaterials at low temperatures – up to the temperature of the liquid hydrogen boiling point) gets at the forefront. It is a very effective method of hydrogen storage with minimum risk.

Storage of high-pressure gaseous hydrogen

The most popular and mature method of hydrogen storage is the storage of gaseous hydrogen in special high-pressure tanks (Zheng et al., 2012) at the pressure of 20 to 30 MPa. However, the volume of hydrogen stored in high-pressure tanks, compared to the tank dimensions, is insufficient, especially when using mobile storage units. So, the hydrogen compression tanks up to more than 70 MPa have been developed (Zheng et al., 2012). This method is convenient for stationary high-pressure gaseous hydrogen storage. In this way, rail and freight transported hydrogen is also stored. Closed pipe systems within industrial objects represent an alternative of gaseous hydrogen transport.

High-pressure storage tanks are multi-layered cylindrical vessels made of anticorrosive materials, mostly of aluminium or stainless steel. Next layer is composed of glass or plastic fibers, or their combination. The cylindrical shape is the most effective for the transmission of stored hydrogen high pressure on the wall of the vessel.

Storage of liquid hydrogen

As summarized by Züttel (2003) and Zhou (2005), to store liquid hydrogen it is necessary to lower its temperature. Cooling of gaseous hydrogen to 23 °K results in its liquefaction, and the change of state reduces stored volume by 99,9 %. To prevent a fast evaporation, it is necessary to store hydrogen in Dewar's vessels. Nevertheless, hydrogen heats up, and released gas must be conveyed.

Other methods of hydrogen storage

Both of above-mentioned hydrogen storage methods are more or less useless for mobile applications or systems, due to the tank weights and relatively small volume of stored gaseous hydrogen and continual loss of stored liquid hydrogen. These disadvantages, as well as progress in hydrogen-based technologies, have led many researchers to look for new methods of hydrogen storage in the last decades (e.g. Kohno et al., 1999; Zaluska et al., 1999; Züttel, 2003; IEA, 2006; Collins, Zhou, 2007; Sakintuna et al., 2007; Murray et al., 2009).

Some metals easily adsorb hydrogen, which molecule dissociates at the surface of the metal and hydrogen atoms penetrate into the metal. In metallic crystalline structure, hydrogen atoms are placed into internode positions (Alefeld, Volkl, 1978; Volkl, Alefeld, 1978).

The most common metal used for hydrogen storage is palladium, which absorbs hydrogen at room temperatures forming palladium hydride (Manchester et al., 1994). However, palladium itself is too expensive and heavy to be used for hydrogen storage. The aim is to look for inexpensive light metals, allowing effective hydrogen storage, such as lithium, alumina, magnesium or rare earth elements. A characteristic feature of hydrogen storage in metal hydrides is the ability to store a relatively large volume of hydrogen compared to volume units. Another feature is its safety. The explosiveness of hydrogen in crystalline structure does not endanger the surroundings.

The limit volume of 6 weight percent storage capacity, from the perspective of stored fuel, is one of request on hydrogen storage methods in mobile applications. Pure magnesium allows to store 7,7 %, what is very high value, but the sorption process is very slow, and magnesium has to be heated to relatively high temperature (Zaluska et al., 1999). So, it is practically inapplicable. In laboratories, lanthanum-pentanickel (LaNi_5) is used. It is possible, in its structure, to store 1,4 weight percent of hydrogen (LaNi_5H_6) (Kristjánssdóttir, Gudmundsdóttir, 2004). This material is used in some technologies, but its use in vehicles, as such heavy fuel tanks, would substantially influence the total weight of the vehicle. Therefore, light metals are subject to intense research, e.g. magnesium and nickel compound – Mg_2Ni , as a potential hydrogen storage medium (Kohno et al., 1996; Sakintuna et al., 2007).

Another possibility of hydrogen storage is adsorption of hydrogen in porous materials with the large specific surface, e.g. carbon nanotube. Nanotubes are of fullerene shape at the bottom.

The rest is of a tube shape. Research results show that this model of hydrogen storage is not absolutely reliable (Lamari Darkrim et al., 2002).

As the nano-scale seems to be relatively well applicable within hydrogen storage, many authors have focused their research on metal-organic framework (e.g.: Rosi et al., 2003; Kesanli et al., 2005; Rowsell, Yaghi, 2005; Latroche et al., 2006; Collins, Zhou, 2007; Dinca, Long, 2008; Murray et al., 2009; Suh et al., 2012). Used light elements (metals and carbon) create atomic like structures with large inner spaces.

Based on above mentioned information, it should be assumed that the following characteristics are crucial for effective hydrogen storage: weight of used materials, the size of free spaces, adsorption and desorption speed of hydrogen.

One of the possible solutions is the use of natural zeolite, as presented in this paper. Zeolites are inert microporous materials, with pore sizes up to 2 nm. These features predetermine them to be used in applications based on large spaces use. Macropores with dimensions of 100 to 200 nm have almost no influence. The specific surface of used zeolite is from 22 to 27 $\text{m}^2\cdot\text{g}^{-1}$.

VAZEP – Large capacity battery for safe and long-term hydrogen storage

Present knowledge, introduced in this paper, has led to research of large capacity battery for hydrogen storage without limitations mentioned in the previous text.

The result of the research is the large capacity battery for safe and long-term hydrogen storage, protected by the utility model no. 59-2012, named as “Veľkokapacitné automatizované zariadenia na uskladňovanie energetických plynov a spôsob ich bezpečného uskladnenia” (VAZEP, English translation: Large Capacity Automotive Device for the Storage of Energy Gasses and Method of Their Safe Storage) (Rybár, Molokáč, 2012).

The device stores hydrogen in inert solid materials (natural zeolites), where, under cryogenic conditions (temperatures of liquid helium), it is possible to fill a storage tank by hydrogen and store it for the long term.

A temperature increase of battery inner space allows hydrogen. Contrariwise, battery re-cooling allows to keep hydrogen in the battery or to refill it. This cycle can be safely repeated for the long term.

The VAZEP device is composed of thermally isolated chamber filled with natural zeolite. Using the thermal key, the chamber is connected or disconnected to/from the cold reservoir and is equipped with regulated heating to be emptied. Device output is connected to the energy gas appliance. The safety of the device is set by high heat capacity and the inertia of zeolites. So, in the case of cooling system failure, there will be no sudden gas leak. The gas will be released gradually (via slow heating of zeolites), so it will be possible to control the hydrogen discharge from the battery.

Gases are stored at cryogenic temperatures under conditions of normal pressure, or higher (up to the critical value), what allows to raise the boiling point of liquid energy gases and reduce operating costs.

Natural zeolite - clinoptilolite and storage of hydrogen in its microstructure

Clinoptilolite (natural zeolite, a sample taken from the Kučín deposit, Slovakia), an inert material with the large inner surface, was used for the experimental study. The sample was milled to obtain a fraction of 0,1 to 1 mm.

Clinoptilolite structure is presented by three-dimensional aluminosilicate framework, whose specific building causes the developed system of micropores and channels occupied by water molecules and exchangeable metal cations (Na, K, Ca, Mg, Fe, Sr, Ba and others). The total volume of pores is 24 to 32 % (Tsitsishvili et al., 1992; Kowalczyk et al., 2006).

Natural zeolites are porous crystalline adsorbents with pores of very uniform size, which is specific for each zeolite type (Ingleziks, Zorpas, 2012). Only materials able to penetrate through pores will be adsorbed into the inner structure of the zeolite. It means that the diameter of penetrating molecules should be smaller than the diameter of zeolite pores.

Storage of hydrogen molecules at surfaces in inner structures of natural zeolite diminishes the distances between molecules of stored liquid energy gas what increases the capacity of stored gas volume.

Based on the documentation from the patent protected utility model (Rybár, Molokáč, 2012), Taylor-Wharton Slovakia Ltd. constructed a prototype of the VAZEP device. Parameters of the device are given in table 1.

Tab. 1. Parameters of VAZEP device prototype.

Weight of the large capacity battery	1600 kg
Outer dimensions (diameter x height)	2 x 2,8 m
Theoretical energy value of the battery	0,9 kW
Theoretical energy power of the system with stored liquid hydrogen	approx. 9 MWh
Interspace vacuum	9 microns ($1,2 \cdot 10^{-5}$ bar)
Volume of the system	1.970 m ³
The bulk density of 1m³ of zeolite	approx. 2700 kg
Zeolite powder density (fraction: 0,1-1 mm)	1,1 kg·dm ⁻¹
Weight of the zeolite in the large capacity battery	1500 kg
Two-stage cooling of the tank and zeolite	1800 l of liquid nitrogen and 500 of liquid helium
Stored material	1600 l of hydrogen, 1600 l of argon

During the long-term test of functionality, following parameters of the device were studied: liquid hydrogen adsorption efficiency of used solid material, functionality of two-stage cooling system, controlling the state changes (liquid and gaseous) of stored gases in real time, operational safety, long-term storage of gases in natural zeolite framework, transfer of evaporated gases from zeolite framework to free space inside the VAZEP and to pressure tanks out of the VAZEP device, filling of VAZEP by cooling, energy, and inert gases, and vacuuming the pressure tank.

To verify the functionality of liquid hydrogen storage using the VAZEP device, following test was performed:

- Step 1: Placing 1500 kg of zeolite powder (fraction: 0,1 – 1 mm) into the pressure tank (Fig. 1)
- Step 2: First stage cooling using liquid nitrogen to reach 77 °K (Fig. 2)
- Step 3: Second-stage cooling using liquid helium to reach 23 °K
- Step 4: Vacuuming of cooled pressure tank
- Step 5: Filling the tank with 1600 l of hydrogen
- Step 6: temperature controlling using liquid helium to cool zeolite
- Step 7: Helium discharge, heating the system
- Step 8: Compressing (20 MPa) of gaseous hydrogen into storage vessels
- Step 9: Vacuuming of pressure vessels
- Step 10: Removal of zeolite powder from the device

Based on the research results obtained during the test of hydrogen storage in a pressure tank filled with 1.363 m³ of natural zeolite (approx. 70 % of the inner volume of the pressure tank), it can be concluded that it is possible to store within inner structure and intergranular spaces of powder zeolite: (1) max. 1.363 m³ of hydrogen, if all the hydrogen will be adsorbed within the inner structure and intergranular spaces of powder zeolite (0,55 + 0,813 m³); (2) min. 0,993 m³ of hydrogen, if all the space above the powder zeolite in the tank will be filled with hydrogen (0,607 m³). However, the real minimum storing volume will be increased by the free space volume above the zeolite in the tank, filled by evaporated (gaseous) hydrogen.

In the free space of the tank, above the zeolite, it is possible to store: (1) max. 0,607 m³ of hydrogen (the volume will be decreased by the volume required for evaporated gaseous hydrogen); (2) min. 0,0 m³ of hydrogen.

Evaporated gaseous hydrogen exhausting was controlled by the pressure sensor, determining the time and volume of exhausted hydrogen into pressure vessels. Temperature and pressure conditions of the system are controlled by the thermal key. Operational safety was ensured by safety valve.

Totally, 1,363 m³ of powder zeolite and 1,6 m³ of hydrogen were stored in the VAZEP device with an inner volume of 1,97 m³. So, 1,5-times more volume of material, compared to the inner device volume, was stored.

The tests, mainly concerning safety, were repeated using another gas – argon. Liquid nitrogen was used for cooling. Tab. 2 shows some important characteristics needed for planning and performing tests using VAZEP device.

Test with argon included the following steps:

- Step 1: Placing 1500 kg of zeolite powder (fraction: 0,1 – 1 mm) into the pressure tank (Fig. 1)
- Step 2: First stage cooling using liquid nitrogen to reach 77 °K (Fig. 2)
- Step 3: Vacuuming of cooled pressure tank
- Step 4: Filling the tank with 2000 l of argon
- Step 5: Temperature controlling (77 °K) using liquid helium to cool zeolite
- Step 6: Heating the system
- Step 7: Compressing of gaseous argon into storage vessels
- Step 8: Vacuuming of pressure vessels
- Step 9: Removal of zeolite powder from the device



Fig. 1. Filling of the VAZEP device with powder zeolite (fraction: 0,1 – 1 mm).



Fig. 2. First-stage cooling (77 °K).

Tab. 2. Important characteristics of cooling liquids and cooled gasses.

	melting point [°K]	boiling point [°K]
Cooling liquids		
helium	0,95	4,22
nitrogen	63,15	77,36
Cooled gasses		
hydrogen	14,01	20,28
argon	83,80	87,30

Considering the technical problems with liquid argon supply, the time gap of 72 hours occurred between first-stage cooling and vacuuming, resulting in moderate zeolite warming and evaporation of 400 l of argon. Thus, the same volume (1,6 m³) of argon, compared to the hydrogen, was in the system.

Obtained results from the test with argon confirmed functionality of the VAZEP device. Used natural zeolite adsorbed the same volumes of argon, as in the case of hydrogen. This model (argon-nitrogen) has several advantages. In laboratories and for experimental studies, it is much safer and significantly cheaper to use argon-nitrogen model than hydrogen-helium. Similarities in thermal characteristic differences of argon-nitrogen and hydrogen-helium models allow to apply the results obtained from the argon model to hydrogen.

Discussion and conclusion

Taking into account the construction of the VAZEP device, it allows safe and long-term storage of energy gases, especially hydrogen. For the storage, the device is based on natural zeolites at cryogenic temperatures (temperatures of liquid helium). In such conditions, it is possible to fill the storage tank with hydrogen and to store it for the long term with minimal loss. Controlled temperature increase within the tank allows drawing off gaseous hydrogen. Re-cooling allows to keep hydrogen in the device or to refill it. This cycle can be safely repeated for the long term.

Safety results from a high heat capacity and inertia of natural zeolites, avoiding any sudden gas leak, even in the case of cooling system crash, as zeolites warm slowly.

Gases are stored at cryogenic temperature, under conditions of normal pressure, or higher (up to critical value), allowing to raise the boiling point of liquid energy gases and reduce operational costs.

Taking into account its safety, the argon-nitrogen model, simulating hydrogen-helium model, is very important further research. This model is advantageous because inner structure of zeolites adsorbs argon molecules similarly as in the case of hydrogen molecules. Also, thermal differences between cooled gases and cooling liquids are similar (tab. 1). It allows to use the thermal key and to apply the results obtained from the argon model to the hydrogen model.

For commercial use, the input of the device will be connected to the gas energy source (supply) and output to energy gas appliance.

Described device and liquid hydrogen storage system are possible to use, besides fuel stations, within the storage system for electricity produced through solar energy. This system will be composed of following technological units: photovoltaic cell ("power plant"), gaseous hydrogen generator, VAZEP device, electricity generator using hydrogen from the VAZEP device, a cryogenic unit for VAZEP cooling, closed cooling water circle to cool other devices.

Here, hydrogen is not the primary source of electricity, but a temporary repository of energy, as it has to be produced by another energy source to be used. However, as an energy storage medium, hydrogen can play a key role in the utilization of renewable energy sources. The presented system of liquid hydrogen storage can balance the current-voltage curve of erratic electricity production, based on the weather, from solar and/or wind power plants. Moreover, system defined in this paper affords the opportunity to store electric energy surplus in the VAZEP device and its selling with profit or during times of wide-scale power outage.

Construction of “island system” will allow using technologies requiring large energy sources at remote places for various purposes, e.g. for drilling narrow vertical boreholes (Rybár et al., 2015) or tourism development in high protected areas (Rybár et al., 2013).

Since it is possible to transport large volume and with sufficient speed and store electric power, it can be assumed, that hydrogen is one of the future energy mediums.

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