

HYDROGEN STORAGE BY CHEMICAL HYDRIDES

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Summary

Among various hydrogen storage methods, this article explains those employing metal hydrides and organic compounds as “hydrogen storage methods using chemical hydrides”. Some methods involving metal hydrides are explained here by comparing the characteristics of MgH_2 , $LaNi_5H_{7.0}$, and Mg_2NiH_4 , etc., with those of gaseous hydrogen and liquid hydrogen, etc., with mention of the general characteristics of metal hydrides, such as heat storage, electricity storage, heating/cooling, etc.

There have been very large numbers of research projects and many reports concerning metal hydrides, some of which are already in practical use. Also explained here are the characteristics and practical uses of organic compounds, including ammonia, methanol, methylcyclohexane, potassium formate, sponge iron and hydrofullerene.

Ammonia, methanol and methylcyclohexane are being studied worldwide together with liquid hydrogen, from the viewpoint of transportation of large quantities of hydrogen for long distances. Development of practically usable methods of employing them is feasible, but research on potassium formate, sponge iron and hydrofullerene is still in the experimental stage, and the future results of this research are eagerly awaited.

1. Metalhydrides, Energy Storage, and Other Applications

Hydrogen can form metal hydrides with some metals and alloys. During the formation of the metal hydride, hydrogen molecules are split and hydrogen atoms are inserted in spaces inside the lattice of suitable metals and/or alloys. In this way an effective storage is created comparable to the density of liquid hydrogen. However, when the mass of the metal or alloy is taken into account then the metal hydride gravimetric storage density is comparable to storage of pressurized hydrogen. The best achievable gravimetric storage density is about 0.07 kg of H₂/kg of metal, for a high temperature hydride such as MgH₂ as shown in Table 1. It gives a comparison of some hydriding substances with liquid hydrogen, gaseous hydrogen, and gasoline.

Medium	Hydrogen content (kg/kg)	Hydrogen storage capacity (kg/L of vol.)	Energy density (kJ/kg)	Energy density (kJ/L of vol.)
MgH ₂	0.070	0.101	9933	14 330
Mg ₂ NiH ₄	0.0316	0.081	4484	11 494
VH ₂	0.0207	—	3831	—
FeTiH _{1.95}	0.0175	0.096	2483	13 620
TiFe _{0.7} Mn _{0.2} H _{1.9}	0.0172	0.090	2440	12 770
LaNi ₅ H _{7.0}	0.0137	0.089	1944	12 630
R.E.Ni ₅ H _{6.5}	0.0135	0.090	1915	12 770
Liquid H ₂	1.00	0.071	141 900	10 075
Gaseous H ₂ (100 bar)	1.00	0.0083	141 900	1170
Gaseous H ₂ (200 bar)	1.00	0.0166	141 900	2340
Gasoline	—	—	47 300	35 500

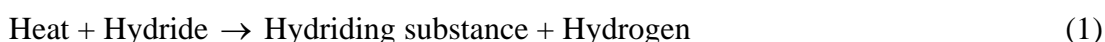
Table 1. Hydriding substances as hydrogen storage media.

During the storage process (charging or absorption) heat is released which must be removed in order to achieve the continuity of the reaction. During the hydrogen release process (discharging or desorption) heat must be supplied to the storage tank.

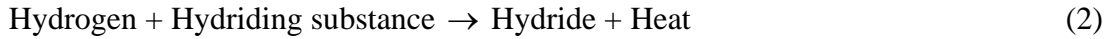
An advantage of storing hydrogen in hydriding substances is the safety aspect. A serious damage to a hydride tank (such as one which could be caused by a collision) would not pose a fire hazard since hydrogen would remain in the metal structure.

1.1 Heat Storage

Any heat, such as waste heat, solar heat and geothermal heat, can be stored as potential hydrogen hydriding energy by supplying the heat to a hydride as shown in the following relationship:



Whenever heat is needed, hydrogen released can be supplied back to the hydride, releasing the hydriding reaction heat, viz.,



If hydrogen is supplied to the hydriding substance at the same pressure as it was released, then the heat released will be at the same temperature (or slightly lower due to the hysteresis effect) as that of the heat supplied. However, by increasing the pressure of the hydrogen supplied, the temperature of the heat released can be increased; and conversely, by reducing the hydrogen pressure, the temperature of the heat released can be reduced. This means that metal hydrides can be used as heat pumps.

1.2 Electricity Storage

Hydriding substances can be used for electricity storage in two ways. In one of the methods, electricity (direct current) is used to electrolyze the water, and the hydrogen produced is stored in a hydriding substance. When electricity is needed, the hydrogen is released from the hydriding substance by adding heat and used in a fuel cell to produce direct current electricity. Heat from the fuel cell can be used to release hydrogen from the metal hydride.

In the second method, the cathode is covered with a hydriding substance (e.g., titanium nickel alloy). During the electrolysis of water, the hydrogen produced on the cathode surface is immediately absorbed by the hydriding substance covering the electrode. Then, when electricity is needed, the electrolyzer operates in a reverse mode as a fuel cell producing electricity using the hydrogen released from the metal hydride.

1.3 Heating/Cooling

Hydrogen, together with hydriding substances, can be used for heating or air-conditioning buildings. Figure 1 shows how one of the proposed systems works. The system consists of four hydride tanks, a solar collector (or a heat source) and a number of heat exchangers. Hydride Tank 1 is connected to hydride Tank 3 with a hydrogen pipe in order to allow the movement of hydrogen from one tank to the other. Similarly, hydride Tanks 2 and 4 are connected in the same fashion. Tanks 1 and 2 contain the same hydriding substance (CaNi_5), and Tanks 3 and 4 contain another hydriding material (LaNi_5). Heat exchangers and the hydride tanks are connected by water-carrying pipe circuits or loops, equipped with a set of switches and valves, so that a hydride tank in a given water loop can be replaced by another hydride tank.

When the system works as a heater, the heat from a heat source (e.g. solar collector) is carried to Tank 1 at about $100\text{ }^\circ\text{C}$ and drives the hydrogen from Tank 1 to Tank 3, where hydrogen is absorbed forming a hydride and heat is released at $40\text{ }^\circ\text{C}$. The water loop carries this heat to the building heat exchangers and heats the air in the building. At the same time, water in the other loop absorbs heat from the ambient and carries it to Tank 4. This heat drives off the hydrogen from Tank 4 to Tank 2 where hydride is formed and heat is generated at $40\text{ }^\circ\text{C}$. The whole operation of driving hydrogen from Tanks 1 and 4 to Tanks 3 and 2 takes about two minutes. At the end of this cycle, the hydride tanks are switched from one loop to the other in Cycle II (as shown in Figure 1). Now the solar heat and the ambient heat are used to drive off the hydrogen in Tanks 2

and 3 to Tanks 4 and 1, respectively. The heat produced during the absorption processes in Tanks 1 and 4 is used for heating the building. After this, the cycles are repeated.

When the system works as an air conditioner, the building heat exchangers are placed in the 8 °C water loop, while the outside heat exchangers are placed in the 40 °C water loops, and operation proceeds in two cycles as described above.

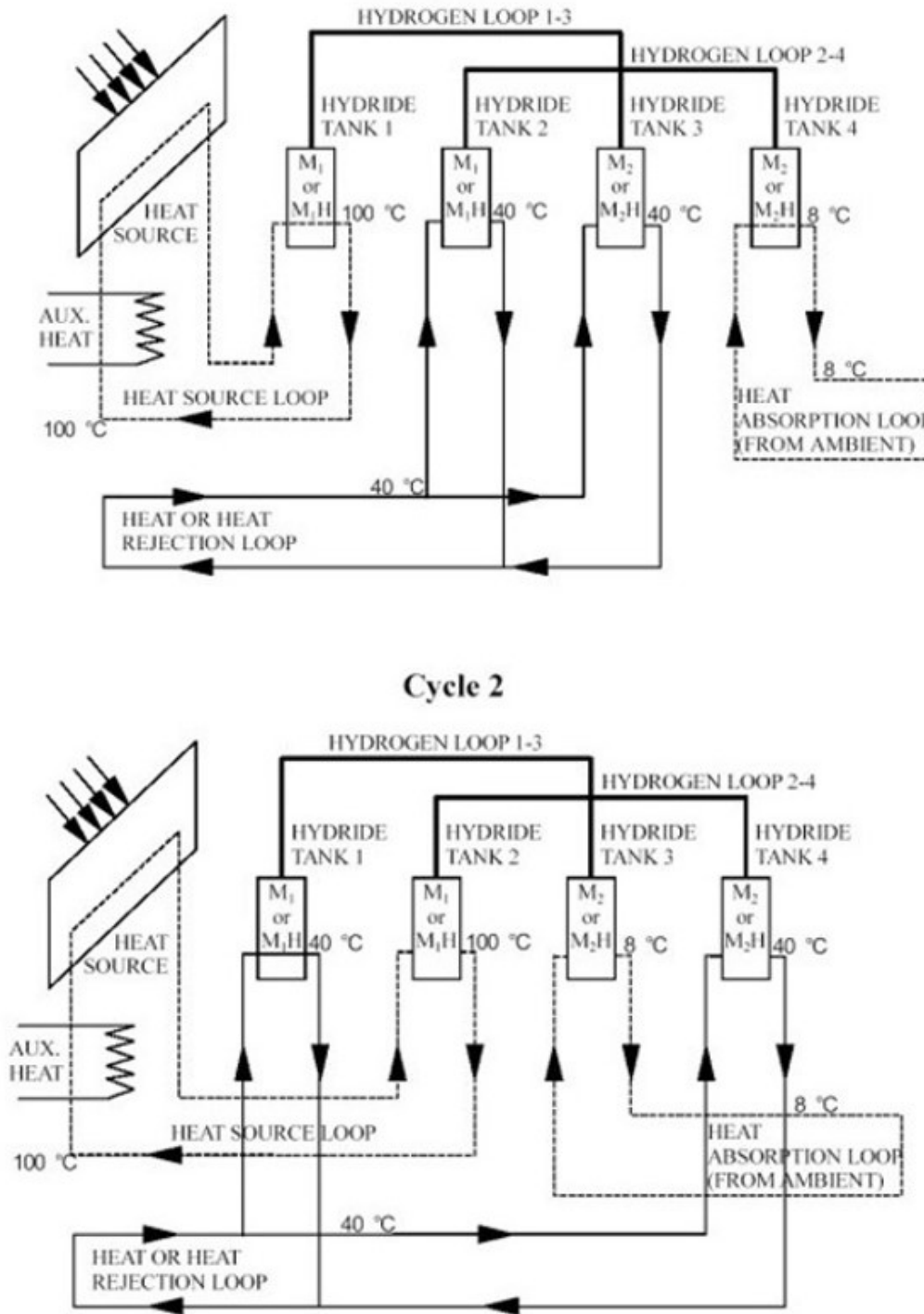


Figure 1. Hydrogen/Hydride Heating-cooling System

1.4 Electricity Generation

If passed through a turbine or expansion engine, hydrogen moving from one hydride tank to the other could produce mechanical and electrical energy, as shown in Figure 2. The system is somewhat similar to the one proposed for heating and cooling. However, it consists of only three tanks containing the same kind of hydriding substance (in this case LaNi_5 , alloy). During the first cycle hydrogen driven off from the desorption tank (Tank 1) by means of solar heat (or heat from any other source) passes through the expansion turbine producing mechanical energy and electricity, and then at a lower pressure is absorbed by the hydriding substance in Tank 2 producing heat at 40°C . In this case, the heat is produced at a lower temperature than the temperature of the desorption since hydrogen is at a lower pressure after passing through the turbine. The heat produced in the absorption tank (Tank 2) is rejected to the environment through the water cooling system. The same water cooling system is also used to cool down the cooling tank (Tank 3) from 100°C to 40°C , since it has served as the desorption tank in the previous cycle. In the second cycle through a system of switches and valves, the tanks are displaced one step to the right in the diagram, i.e., the cooling tank becomes the absorption tank, the absorption tank becomes the desorption tank, and the desorption tank becomes the cooling tank. Then, the cycles are repeated. Using this method, low quality heat could be converted to electricity.

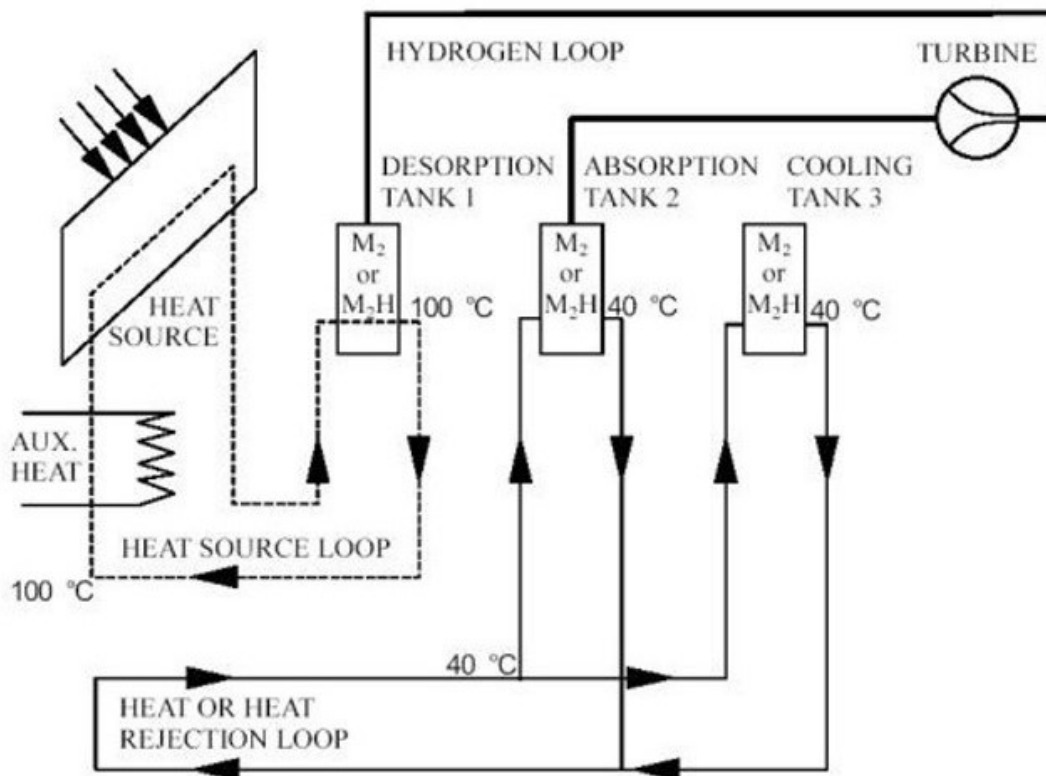


Figure 2. Electricity Generation via Hydrogen and Hydrides

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Biographical Sketch

Kunihiro Takahashi was born 28 January 1942 in Japan; he graduated from Chemical System Engineering Department, Faculty of Engineering, the University of Tokyo; completed 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: appointed as a member of General Research Laboratory of Tokyo Gas Co., Ltd. (1967–1977); appointed as 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); appointed as a member of Sub-task-1-committee of WE-NET committee of New Energy and Industrial Technology Development Organization (1994–1997). He has held present position since June 1997; studied research themes: production processes and catalysts for hydrogen-rich gas and methane-rich gas.