REVIEW OF HYDROGEN CONVERSION TECHNOLOGIES

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Abstract: Hydrogen can be converted into useful forms of energy in several ways. Some of hydrogen conversion technologies are unique to hydrogen, but all of them are more efficient and less polluting than conversion of conventional fuels. This paper reviews hydrogen conversion technologies such as combustion in internal combustion engines, hydrogen/oxygen combustion for steam generation, catalytic combustion, electrochemical conversion in fuel cells and metal hydride technologies.

Key words: hydrogen, combustion, internal combustion engines, catalytic combustion, fuel cells, metal hydrides

Introduction

Hydrogen and electricity are often considered as complementary energy carriers for the future. Hydrogen has some unique properties, which in conjunction with electricity make it an ideal energy carrier or fuel [1,2]:

- Just as electricity hydrogen can be produced from any energy source, including the renewable energy sources.
- Hydrogen can be produced from electricity and can be converted into electricity at relatively high efficiencies. Some processes for hydrogen production directly from solar energy are also being developed, such as photo-electro-chemical conversion or biological photo-production.
- Raw material for hydrogen production is water, which is available in abundance. Hydrogen is a completely renewable fuel, since the product of hydrogen utilization (either through combustion or through chemico-electrical conversion) is pure water or water vapor.
- It can be stored in gaseous form (convenient for large scale storage), in liquid form (convenient for air and space transportation) or in the form of metal hydrides (convenient for surface vehicles and other relatively small scale storage requirements).
- It can be transported over large distances through pipelines or via tankers (in most of the cases more efficiently and economically than electricity).
- It can be converted into other forms of energy in more ways and more efficiently than any other fuel, e.g., through catalytic combustion, electro-chemical conversion and hydriding, as well as through flame combustion.
- Hydrogen as an energy currency is environmentally compatible, since its production from electricity (or directly from solar energy), its storage and transportation, and its end use do not produce any pollutants (except some NO_X if hydrogen is burned with air) or any other harmful effects on the environment. It also does not produce any greenhouse gases, particularly CO_2.

Hydrogen and electricity would form a permanent energy system independent of energy sources. The key technologies in such an energy system are technologies for hydrogen production, storage, transportation and utilization. This paper presents a review of technologies for hydrogen conversion

into the useful forms of energy These technologies, already developed and demonstrated, will enable hydrogen's widespread use in the future., such as thermal, mechanical and electrical energies.

Combustion of hydrogen in internal combustion engines and turbines

Hydrogen is a very good fuel for internal combustion engines. Hydrogen powered internal combustion engines are on average about 20% more efficient than comparable gasoline engines. The ideal thermal efficiency of an internal combustion engine is:

$$\eta = 1 - \left(\frac{1}{r}\right)^{k-1} \qquad\qquad (1)$$

where:
r = compression ratio, and
k = ratio of specific heats (C_p/C_v).

This equation shows that the thermal efficiency can be improved by increasing either the compression ratio or the specific heat ratio. In hydrogen engines both ratios are higher than in a comparable gasoline engine due to hydrogen's lower self-ignition temperature and ability to burn in lean mixtures. However, the use of hydrogen in internal combustion engines results in loss of power due to lower energy content in a stoichiometric mixture in the engine's cylinder. A stoichiometric mixture of gasoline and air and gaseous hydrogen and air pre-mixed externally occupy ~2% and 30% of the cylinder volume, respectively. Under these conditions, the energy of the hydrogen mixture is only 85% of the hydrogen mixture, thus resulting in about 15% reduction in power. Therefore, the same engine running on hydrogen will have ~15% less power than when operated with gasoline. The power output of a hydrogen engine can be improved by using more advanced fuel injection techniques or liquid hydrogen. For example, if liquid hydrogen is premixed with air, the amount of hydrogen that can be introduced in the combustion cylinder can be increased by approximately one-third [3].

One of the most important advantage of hydrogen as a fuel for internal combustion engines is that hydrogen engines emit by far fewer pollutants than comparable gasoline engines. Basically, the only products of hydrogen combustion in air are water vapor and small amounts of nitrogen oxides. Hydrogen has a wide flammability range in air (5 to 75% vol.) and therefore high excess air can be utilized more effectively. The formation of nitrogen oxides in hydrogen/air combustion can be minimized with excess air. NO_x emissions can also be lowered by cooling the combustion environment using techniques such as water injection, exhaust gas recirculation, or using liquid hydrogen. The emissions of NO_x in hydrogen engines are typically one order of magnitude smaller than emissions from comparable gasoline engines. Small amounts of unburned hydrocarbons, CO_2, and CO have been detected in hydrogen engines due to lubrication oil [3].

The low ignition energy and fast flame propagation of hydrogen has led to problems of pre-ignition and backfire. These problems have been overcome by adding hydrogen to the air mixture at the point where and when the conditions for pre-ignition are less likely, such as delivering the fuel and air separately to the combustion chamber, and/or injecting hydrogen under pressure into the combustion chamber before the piston is at the top dead center and after the intake air valve has been closed. Water injection and exhaust gas recirculation techniques are

also used in hydrogen engines to help control premature ignition. It should be noted that most of the research oh hydrogen combustion in internal combustion engines has been conducted with modifications of existing engines designed to burn gasoline. Redesign of the combustion chamber and coolant systems to accommodate hydrogen's unique combustion properties could be the most effective method of solving the problems of preignition and knocking [3].

Hydrogen use in turbines and jet engines is similar to use of conventional jet fuel. The use of hydrogen avoids the problems of sediments and corrosion on turbine blades which prolongs life and reduces maintenance. Gas inlet temperatures can be pushed beyond normal gas turbine temperatures of 800 °C, thus increasing the overall efficiency. The only pollutants resulting from the use of hydrogen in turbines and jet engines are nitrogen oxides.

Hydrogen has traditionally been used in the space program as fuel for the rocket engines of launch vehicles. The space programs are currently the biggest consumer of liquid hydrogen. A tremendous body of experience in handling liquid hydrogen has been gained as a result of the development and use of liquid hydrogen/liquid oxygen fueled rocket engines in the space program, including manufacture and liquefaction of hydrogen, as well as transportation, storage, pipelining, instrumentation, design practices, operational use, and safety procedures. This experience may be a basis for development of other hydrogen technologies and their expansion in other energy markets.

Direct steam generation by hydrogen/oxygen combustion

Hydrogen combusted with pure oxygen results in pure steam, i.e.,:

$$2H_2 + O_2 \rightarrow 2H_2O \qquad\qquad\qquad (2)$$

The above reaction would develop temperatures in the flame zone above 3,000 °C, therefore, additional water has to be injected so that the steam temperature can be regulated at a desired level. Both saturated and superheated vapor can be produced.

The German Aerospace Research Establishment (DLR) has developed a compact hydrogen/ oxygen steam generator [4]. The steam generator consists of the ignition, combustion and evaporation chambers. In the ignition chamber a combustible mixture of hydrogen and oxygen at a low oxidant/fuel ratio is ignited by means of a spark-plug. The rest of oxygen is added in the combustion chamber to adjust the oxidant/fuel ratio exactly to the stoichiometric one. Water is also injected in the combustion chamber after it has passed through the double walls of the combustion chamber. The evaporation chamber serves to homogenize the steam. The steam's temperature is monitored and controlled. Such a device is close to 100% efficient, since there are no emissions other than steam and little or no thermal losses.

The hydrogen steam generator can be used to generate steam for spinning reserve in power plants, for peak load electricity generation, in industrial steam supply networks and as a micro steam generator in medical technology and biotechnology [4].

Catalytic combustion of hydrogen

Hydrogen and oxygen in presence of a suitable catalyst may be combined at temperatures significantly lower than flame combustion (from ambient to 500 °C). This principle can be used to design catalytic burners and heaters. Catalytic burners require considerably more surface area than conventional flame burners. Therefore, the catalyst is typically dispersed in a porous structure. The reaction rate and resulting temperature are easily controlled by controlling the hydrogen flow rate. The reaction takes place in a reaction zone of the porous catalytic sintered metal cylinders or plates in which hydrogen and oxygen are mixed by diffusion from opposite sides. A combustible mixture is formed only in the reaction zone and assisted with (platinum) catalyst to burn at low temperatures (Figure 1). The only product of catalytic combustion of hydrogen is water vapor. Due to low temperatures there are no nitrogen oxides formed. The reaction cannot migrate into the hydrogen supply, since there is no flame and hydrogen concentration is above the higher flammable limit (75%).

Possible applications of catalytic burners are in household appliances such as cooking ranges and space heaters. The same principle is also used in hydrogen sensors.
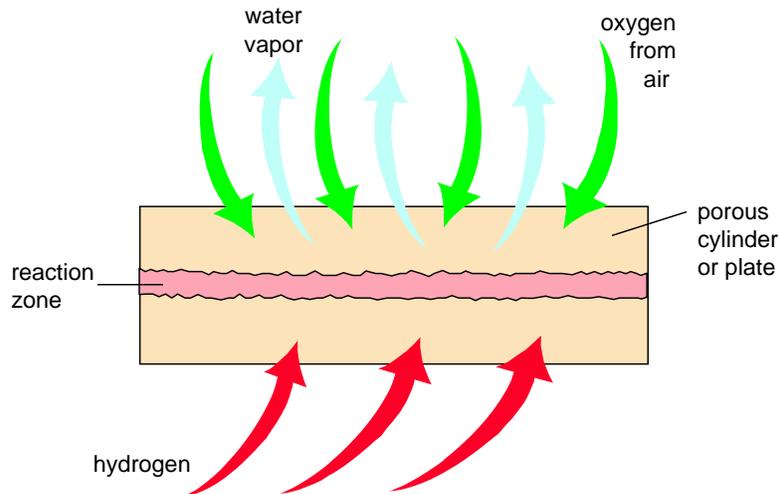
Figure 1 Schematic representation of catalytic burner

Electrochemical electricity generation (fuel cells)

Hydrogen can be combined with oxygen without combustion in an electrochemical reaction (reverse of electrolysis) and produce electricity (DC). The device where such a reaction takes place is called the electrochemical fuel cell or just fuel cell.

Depending on the type of the electrolyte used, there are several types of fuel cells:

- Alkaline fuel cells (AFC) use concentrated (85 wt%) KOH as the electrolyte for high temperature operation (250°C) and less concentrated (35-50 wt%) for lower temperature operation (<120°C). The electrolyte is retained in a matrix (usually asbestos), and a wide

range of electrocatalysts can be used (such as Ni, Ag, metal oxides, and noble metals). This fuel cell is intolerant to CO_2 present in either fuel or oxidant [5].

- Polymer electrolyte membrane or proton exchange membrane fuel cells (PEMFC) use a thin polymer membrane (such as perfluorosulfonated acid polymer) as the electrolyte. The membranes as thin as 12-20 microns have been developed, which are excellent proton conductors. The catalyst is typically platinum with loadings about 0.3 mg/cm^2, or, if the hydrogen feed contains minute amounts of CO, Pt-Ru alloys are used. Operating temperature is usually below 100°C, more typically between 60 and 80°C.
- Phosphoric acid fuel cells (PAFC), use concentrated phosphoric acid (~100%) as the electrolyte. The matrix used to retain the acid is usually SiC, and the electrocatalyst in both the anode and cathode is Platinum black. Operating temperature is typically between 150-220°C [5,6].
- Molten carbonate fuel cells (MCFC) have the electrolyte composed of a combination of alkali (Li, Na, K) carbonates, which is retained in a ceramic matrix of $LiAlO_2$. Operating temperatures are between 600-700°C where the carbonates form a highly conductive molten salt, with carbonate ions providing ionic conduction. At such high operating temperatures, noble metal catalysts are typically not required [5,6].
- Solid oxide fuel cells (SOFC) use a solid, nonporous metal oxide, usually Y_2O_3-stabilized ZrO_2 as the electrolyte. The cell operates at 900-1000°C where ionic conduction by oxygen ions takes place [5,6].

A typical fuel cell consists of the electrolyte in contact with a porous electrodes on both sides. A schematic representation of a fuel cell with reactant and product gases, and ions flow directions for the major types of fuel cells are shown in Figure 2. The electrochemical reactions occur at the three-phase interface - porous electrode/electrolyte/ reactants.
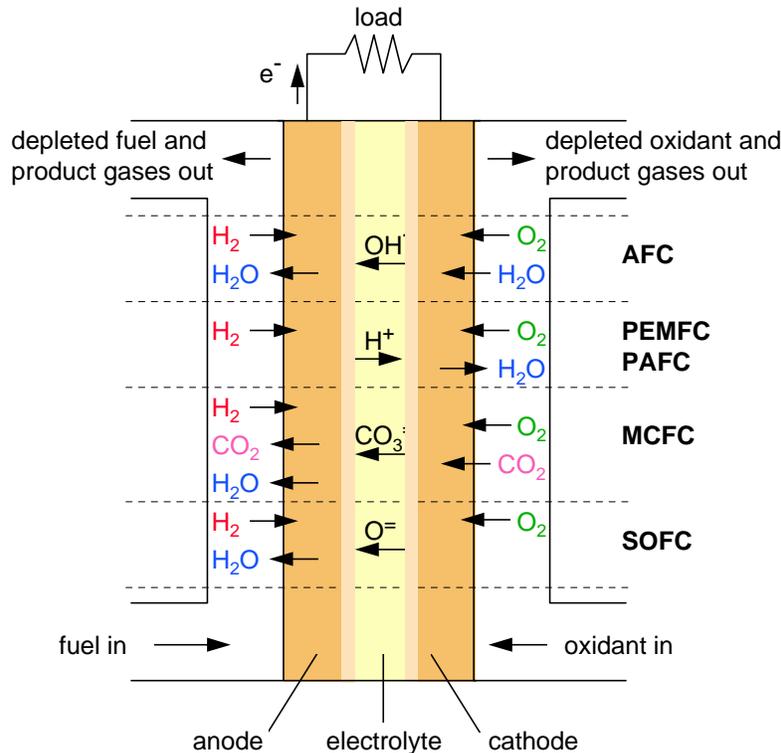
Figure 2 Operating principle of various types of fuel cells

The actual electrochemical reactions that occur in the above listed types of fuel cells are different (as shown in Table 1) although the overall reaction is the same, i.e., $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$. Low temperature fuel cells (AFC, PEMFC, PAFC) require noble electrocatalysts to achieve practical reaction rates at the anode and cathode. High temperature fuel cells (MCFC and SOFC) can also utilize CO and CH_4 as fuels. The operating temperature is high enough so that CO and CH_4 can be converted in hydrogen through the water-gas shift and steam reforming reactions respectively.

The electrolyte not only transports dissolved reactants to the electrode, but it also conducts ionic charge between the electrode and thereby completes the cell electric circuit, as shown in Figure 2.

Table 1. Fuel Cell Reactions

Fuel Cell Type	Anode Reaction	Cathode Reaction
Alkaline	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$
Proton Exchange	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Phosphoric Acid	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Molten Carbonate	$H_2 + CO_3^= \rightarrow H_2O + CO_2 + 2e^-$	$\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^=$
Solid Oxide	$H_2 + O^= \rightarrow H_2O + 2e^-$	$\frac{1}{2}O_2 + 2e^- \rightarrow O^=$

The reversible potential of the above electrochemical reactions is 1.229 V (at standard conditions, i.e., 25 °C and atmospheric pressure), and it corresponds to the Gibbs free energy according to the following equation:

$$\Delta G^o = nFE^o \tag{3}$$

where:
ΔG^o = Gibbs free energy at 25°C and atmospheric pressure
n = number of electrons involved in the reaction
F = Faraday's constant
E^o = reversible potential at 25°C and atmospheric pressure (V)

The reversible potential changes with temperature and pressure; in general it is lower at higher temperatures (reaching ~1.0 V at 1000 K), and it is higher at higher pressures or higher concentrations of reactants. The actual voltage of an operational fuel cell is always lower than the reversible potential due to various irreversible losses, such as activation polarization, concentration polarization and ohmic resistance. While ohmic resistance is directly proportional to the current, activation polarization is a logarithmic function of current, and thus more pronounced at very low current densities, and concentration polarization is an exponential function of current and thus becomes a limiting factor at high current densities. Figure 3 shows a typical fuel cell polarization curve with pronounced regions of predominant irreversible losses. Figure 4 shows actual polarization curves of some representative fuel cells. The fuel cells are typically operated in a range between 0.6 and 0.8 V. The Space Shuttle fuel cell (alkaline) is

designed to operate at 0.86 V and 410 mA/cm^2 [5]. PEM fuel cells have the highest achievable current densities, between 1 and 2 mA/cm^2 at 0.6 V with pressurized hydrogen and air.
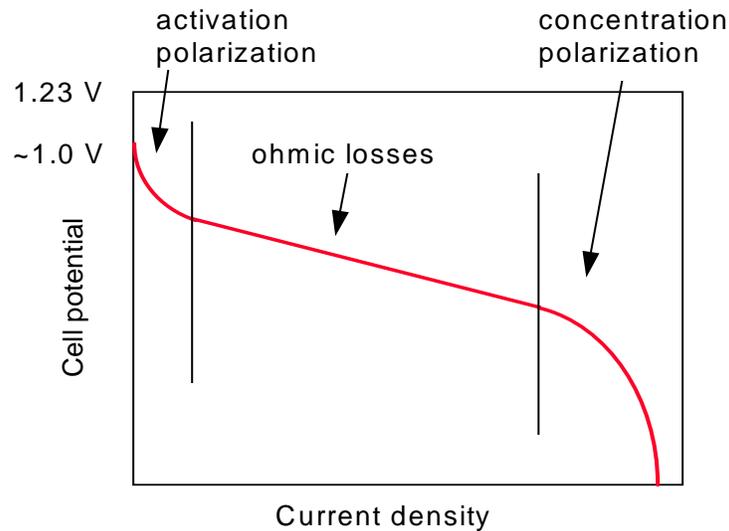
Figure 3 Typical fuel cell polarization curve
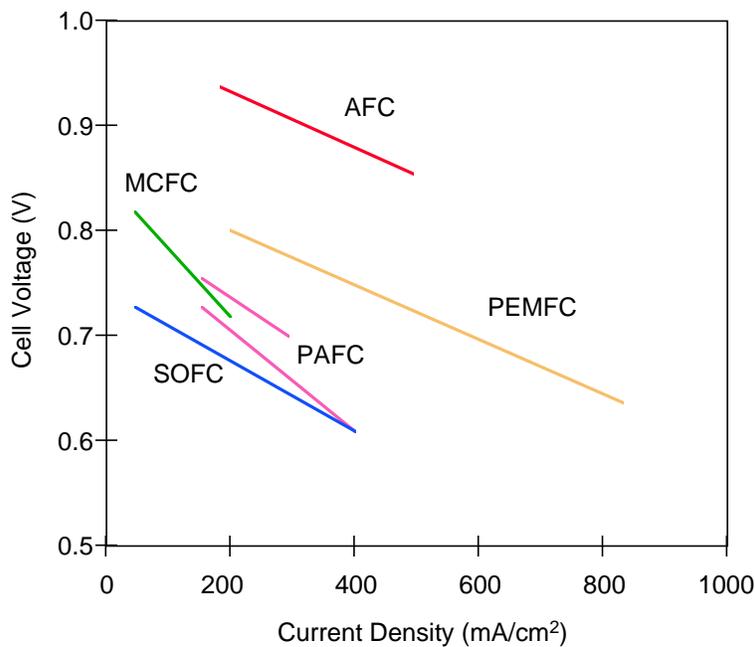
Figure 4 Polarization curves of some representative fuel cells
AFC - United Technologies' fuel cell operating in Space Shuttle, with H$_2$ and O$_2$ at 80-90°C, 410 kPa
PEMFC - Ballard's 25 kW fuel cell operating in Daimler-Benz vehicle (NECAR II) with H$_2$ and air
PAFC - IFC's fuel cell operating in ONSI PC25 200 kW power plant, operating on reformed natural gas and air at atmospheric pressure (1996); (upper line is IFC's PC23 operating at 820 kPa)
MCFC - ERC's atmospheric pressure fuel cell operating with natural gas (1994)
SOFC - Westinghouse fuel cell operating at atmospheric pressure using natural gas (1991)

The fuel cell efficiency is a function of cell voltage. The theoretical fuel cell efficiency is:

$$\eta_{FC} = \Delta G / \Delta H \qquad (4)$$

where ΔH is hydrogen's enthalpy or heating value (higher or lower). The theoretical fuel cell efficiency, defined as a ratio between produced electricity and higher heating value of hydrogen consumed is therefore 83%. The lower heating value of hydrogen results in an efficiency of 98%. Since the actual voltage of an operational fuel cell is lower than the reversible potential, the fuel cell efficiency is always lower than theoretical. Generally, the fuel cell efficiency is a product of several efficiencies:

$$\eta_{FC} = \eta_{Th} \cdot \eta_V \cdot \eta_F \cdot \eta_U \qquad (5)$$

where:

η_{Th} = thermal efficiency, i.e., ratio between Gibbs free energy of the reaction and heating value of the fuel, $\Delta G_r / \Delta H_{fuel}$ (similarly to internal combustion engines, the fuel cell efficiency is often expressed in terms of lower heating value)

η_V = voltage efficiency, defined as a ratio between actual voltage (V) and thermodynamic voltage (E), i.e., V/E

η_F = Faradaic efficiency, or ratio between the actual current and current corresponding to the rate at which the reactant species are consumed, I/nFm, where m is the rate (in moles/s) at which the reactants are consumed.

η_U = fuel utilization, or ratio between the amount of fuel actually consumed in the electrochemical reaction and fuel supplied to the fuel cell.

For a hydrogen/oxygen or hydrogen/air fuel cell operating with 100% fuel utilization, the efficiency is a function of cell voltage only. For such a fuel cell the efficiency in an operating range between 0.6 V and 0.8 V is between 0.48 and 0.64. In order to get useable voltages (i.e., tens or hundred Volts), the cells are combined in a stack. The cells are physically separated from each other and electrically connected in series by a bipolar separator plate. Figure 5 shows a schematic representation of a typical fuel cell stack.
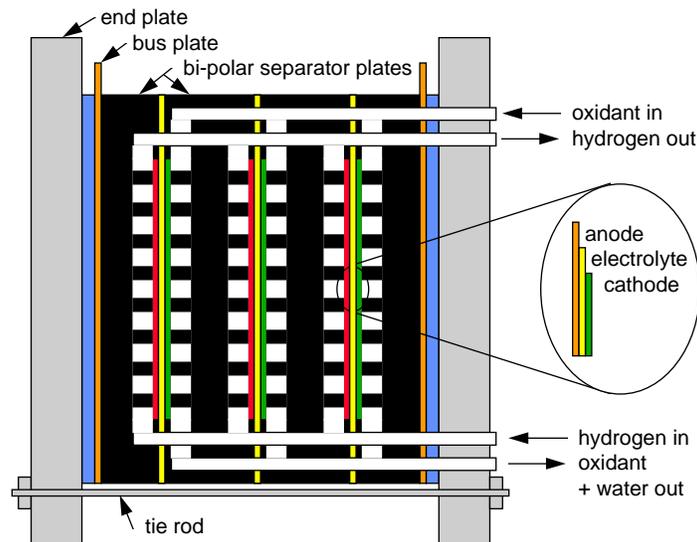
Figure 5 Schematic representation of a typical fuel cell stack

Alkaline fuel cells have been used in the space program (Apollo and Space Shuttle) since 1960's. Phosphoric acid fuel cells are already commercially available in container packages for stationary electricity generation. PEM fuel cells are a serious candidate for automotive applications, but also for small scale distributed stationary power generation. High temperature fuel cells, such as molten carbonate and solid oxide fuel cells, have been developed to a precommercial/ demonstration stage for stationary power generation.

Metal hydrides applications

Hydrogen's property to form metal hydrides may be used not only for hydrogen storage but also for various energy conversions. When a hydride is formed by the chemical combination of hydrogen with a metal, an element or an alloy, heat is generated, i.e., the process is exothermic. Conversely, in order to release hydrogen from a metal hydride heat must be supplied. These processes can be represented by the following chemical reactions:

$$Charging \ or \ absorption: \qquad M + xH_2 \rightarrow MH_{2x} + heat \qquad\qquad (6)$$

$$Discharging \ or \ desorption: \qquad MH_{2x} + heat \rightarrow M + xH_2 \qquad\qquad (7)$$
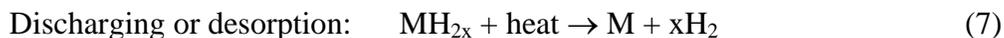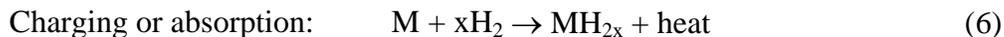
where M represents the hydriding substance, a metal, an element or an alloy. The rate of these reactions increase with increase in the surface area. Therefore, in general, the hydriding substances are used in powdered form to speed up the reactions.

Elements or metals with unfilled shells or subshells are suitable hydriding substances. Metal and hydrogen atoms form chemical compounds by sharing their electrons in the unfilled subshells of the metal atom and the K shells of the hydrogen atoms.

Ideally, for a given temperature, the charging or absorption process and the discharging or desorption process takes place at the same constant pressure. However, actually, there is a hysteresis effect and the pressure is not absolutely constant - for a given temperature charging pressures are higher than the discharging pressures. The heat generated during the charging process and the heat needed for discharging are functions of the hydriding substance, the hydrogen pressure and the temperature at which the heat is supplied or extracted. Using different metals and by forming different alloys, different hydriding characteristics can be obtained. In other words, it is possible to make or to find hydriding substances which are more suitable for a given application, such as waste heat storage, electricity generation, pumping, hydrogen purification and isotope separation.

Hydrogen storage

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 such a 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 H_2/kg of metal, for a high temperature hydride such as MgH_2 as shown in Table 2. It gives a comparison of some hydriding substances with liquid hydrogen, gaseous hydrogen and gasoline [7].

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 the one which could be caused by a collision) would not pose fire hazard since hydrogen would remain in the metal structure.

Table 2. Hydriding Substances as Hydrogen Storage Media

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	9,933	14,330
Mg_2NiH_4	0.0316	0.081	4,484	11,494
VH_2	0.0207		3,831	
$FeTiH_{1.95}$	0.0175	0.096	2,483	13,620
$TiFe_{0.7}Mn_{0.2}H_{1.9}$	0.0172	0.090	2,440	12,770
$LaNi_5H_{7.0}$	0.0137	0.089	1,944	12,630
$R.E.Ni_5H_{6.5}$	0.0135	0.090	1,915	12,770

<u>Heat storage</u>

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:

$$\text{Heat + Hydride} \longrightarrow \text{Hydriding substance + Hydrogen} \qquad (8)$$

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

$$\text{Hydrogen + Hydriding substance} \longrightarrow \text{Hydride + Heat} \qquad (9)$$
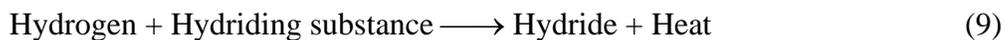
If hydrogen is supplied to the hydriding substance at the same pressure as it was released, than the heat released will be at the same temperature (or slightly lower due to the hysteresis effect) as that of the heat supplied. However, by increasing the pressure of the hydrogen supplied, the temperature 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.

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 fuel cell can be used to release hydrogen from the metal hydride. In the second method, one electrode is covered with a hydriding substance (e.g., titanium nickel alloy). During the electrolysis of water, the hydrogen produced on the electrode 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.

Heating/Cooling

Hydrogen together with hydriding substances can be used for heating or air-conditioning the buildings. Figure 6 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 heater, the heat from a heat source (e.g. solar collector) is carried to Tank 1 at about 100°C and drives the hydrogen from Tank 1 to Tank 3, where hydrogen is absorbed forming a hydride and heat is released at 40°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°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 6) 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.

HYDROGEN LOOP 1-3

HYDROGEN LOOP 2-4

HEAT SOURCE

AUX. HEAT

HYDRIDE TANK 1
M_1 or M_1H 100℃

HYDRIDE TANK 2
M_1 or M_1H 40℃

HYDRIDE TANK 3
M_2 or M_2H 40℃

HYDRIDE TANK 4
M_2 or M_2H 8℃

100℃

HEAT SOURCE LOOP

8℃

HEAT ABSORPTION LOOP (FROM AMBIENT)

40℃

HEAT OR HEAT REJECTION LOOP

Cycle I

HYDROGEN LOOP 1-3

HYDROGEN LOOP 2-4

HEAT SOURCE

AUX. HEAT

HYDRIDE TANK 1
M_1 or M_1H 40℃

HYDRIDE TANK 2
M_1 or M_1H 100℃

HYDRIDE TANK 3
M_2 or M_2H 8℃

HYDRIDE TANK 4
M_2 or M_2H 40℃

100℃

HEAT SOURCE LOOP

8℃

HEAT ABSORPTION LOOP

40℃

HEAT OR HEAT REJECTION LOOP

Cycle II

Figure 6 Hydrogen/Hydride Heating-Cooling System

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 7. 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.

HYDROGEN LOOP   TURBINE

DESORPTION   ABSORPTION   COOLING
TANK 1   TANK 2   TANK 3
M$_2$ or M$_2$H   M$_2$ or M$_2$H   M$_2$ or M$_2$H
100℃   40℃   40℃

HEAT SOURCE

AUX. HEAT
100℃   HEAT SOURCE LOOP

40℃

HEAT OR HEAT REJECTION LOOP
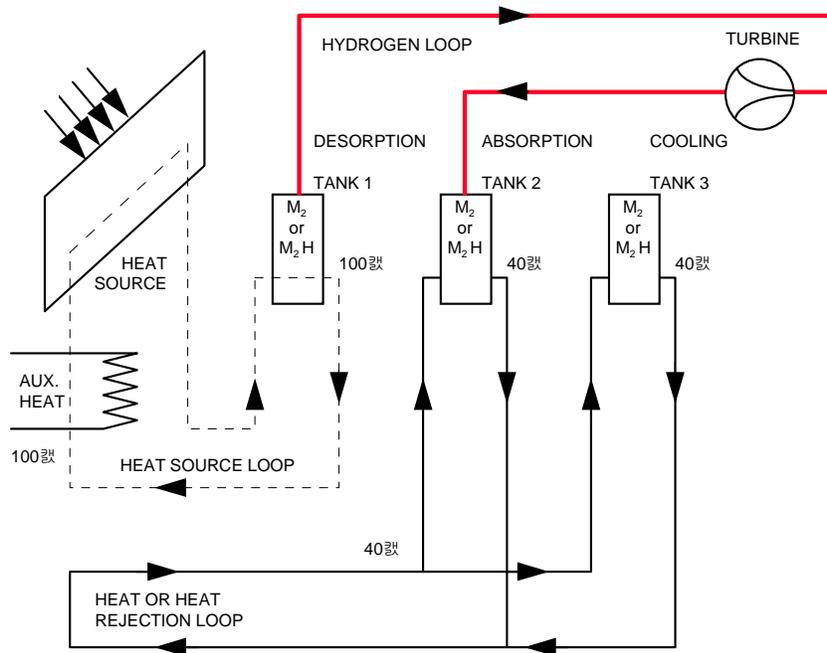
Figure 7 Electricity generation via hydrogen and hydrides

Pumping or pressurizing

The relationship between the hydrogen pressure (p) and the hydride temperature (T) in the absorption or desorption process is given by the following equation:

$$p = exp\left(\frac{\Delta H}{RT} + S\right) \tag{10}$$

where ΔH is the hydriding reaction enthalpy, R the gas constant, and S a constant depending on the hydriding substance. If the hysteresis is neglected, the above equation would hold for both the absorption and desorption processes. By using heat it would be possible to increase hydrogen pressure by a hundred or more times. The pressure ratio would be:

$$\frac{p_{Hi}}{p_{Lo}} = exp\left[\frac{\Delta H}{R}\left(\frac{1}{T_{Hi}} - \frac{1}{T_{Lo}}\right)\right] \qquad (11)$$

where P_{Hi} is the hydrogen pressure corresponding to the hydride temperature T_{Hi} , and P_{Lo} is the hydrogen pressure corresponding to the hydride temperature T_{Lo}.

Hydrogen purification

In many applications, such as the hydrogenation of vegetable oils and some laboratory experiments, high purity hydrogen is needed. One property of the hydriding substances is that they absorb hydrogen but not the other elements or molecules which may be present as impurities. Using this property of the hydriding substances, it is possible to purify hydrogen simply and inexpensively. A hydride tank is first charged with impure hydrogen while heat is being removed. Only hydrogen forms hydride, which allows impurities to be flushed from the hydride tank. Once the impurities are flushed from the tank, heat may be applied and pure hydrogen is released from the hydride. For continuous operation, the system may be equipped with three tanks (absorption, flushing and desorption) and their roles can be switched in cycles.

Deuterium separation

The property of hydrides used for hydrogen purification, can also be used for deuterium separation. The system is similar to the hydrogen purification system. Deuterium is flushed from the hydriding tank, while hydrogen remains bonded in the metal hydride. Using titanium nickel alloy as the hydriding substance, it is possible to obtain 85% pure deuterium after only two steps. With three and four steps, it is possible to obtain 99.9% and 99.999% pure deuterium respectively.

Conclusion

Although a majority of the above described hydrogen conversion technologies has already been developed and demonstrated, and most of them has a clear advantage over the existing technologies, hydrogen is not being used as a fuel on a large scale (except for the space programs). The reasons are various and complex, and include not only technical but economical and political aspects, addressing of which is outside the scope ot this paper.

Hydrogen as a fuel must be considered in a frame of the entire energy system. Technologies for hydrogen utilization must be accompanied by the equally viable technologies for hydrogen production, storage, transportation and distribution. Consideration of an individual hydrogen energy technologiy outside the context of the complete hydrogen energy system creates an incomplete and most often skewed picture. It is often possible to find another technology that may be either better, or less expensive, or more efficient, or more convenient, but there is no other energy system (at least not based on presently known technologies) that can compare with the benefits that the hydrogen energy system offers.

Hydrogen energy system is a coherent, comprehensive and permanent solution to global energy-economic-environmental problems, and as such deserves support from individual governments and industrial organizations. Hydrogen energy technologies are particularly interesting for the developing countries that do not have huge energy infrastructures in place. These countries do

not have to follow industrialization path of the developed countries by building huge power plants, power transmission lines, pipelines, transportation infrastructure, energy intensive industries, etc., and creating environmental problems associated with such development. Development of an energy infrastructure for an energy system that will not last long anyway, does not make much sense. Instead, those countries may adopt a "softer" path by relying more on dispersed renewable energy sources and both traditional and advanced technologies for their utilization. Introduction of modular and portable fuel cell power systems, for example, seems to be a viable alternative. Although initially these new technologies may be more expensive in the long run they are definitely beneficial to both economy and the environment.

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