Chapter 6

Novel Applications of the Developed Materials

Abstract

This chapter discusses novel applications of the developed metal hydrides. These are hydrogen storage, fuel storage (stationary and vehicular applications), electrical energy storage (battery and fuel cell applications), thermodynamic devices (heat pump, refrigerator and compressor) and other applications (catalysts for hydrogen reduction, sensor devices and purification).

6.1 Introduction

Metal hydrides are easily reversible at moderate temperatures (250 K – 600 K) and pressures (0.1 bar – 100 bar) and they have stimulated much interest for their use in various energy storage and conversion systems [1]. A brief review is given here of various niche applications of the metal hydrides.

6.2 Hydrogen Storage

Molecular hydrogen is “absorbed” in hydride-forming metals and alloys in the crystalline lattice as mono-atomic hydrogen to form metal hydrides and it is “desorbed” from the crystalline lattice to return to molecular hydrogen [2]. The mono-atomic hydrogen sites in the crystalline lattice are the source of hydrogen stored as given in Eqn. 6.1:

$$H_2 \longleftrightarrow 2H^\circ \text{ (protium in crystalline lattice)} \quad \text{--------------------- (6.1)}$$

Many of the intermetallic compounds and solid-solution alloys can readily absorb and desorb hydrogen gas around room temperature and near atmospheric H_2 pressures [3]. Serious efforts to increase the capacity of these low temperature metal hydrides have been made. The maximum hydrogen storage capacity of low temperature metal hydrides still remains below 2 mass % of H_2, which is not enough for most vehicle applications [4]. On the other hand, covalent hydride (MgH_2) is capable of storing 7.66 mass % of H_2, but they must be heated above 600 K to release gas at a pressure of 1 bar. These desorption temperatures are much higher than the 350 K waste heat available from an exhaust fuel gases or a Proton Exchange Membrane (PEM) fuel cell. However, recent progress has been with “catalyzed” complex hydrides containing mixed ionic-covalent bonding which can reversibly store > 4 mass % of H_2 with operating temperatures below 400 K [5, 6].

The volume required for 1 kg of hydrogen storage in gaseous phase at standard atmospheric pressure and temperature is equal to 11, 236 litre. But, commercially available hydrogen cylinder is pressurized up to 150 kg/cm^2. Therefore, the required volume for 1 kg hydrogen is 75 litre at 150 kg/cm^2. Low temperature based alloy compositions (V based) have reversible minimum 1.0 mass % of H_2 storage capacity and apparent density is 2.64 gm/cm^3. Assume maximum volume growth during absorption is 30 %. Therefore, for 1 kg of hydrogen storage, required volume of low temperature based metal hydride (V based) is 38 litre. Mg based alloy compositions have reversible minimum 6 mass % of H_2 storage capacity. The apparent density of Magnesium hydride is 0.9809 gm/cm^3. Assume maximum volume growth during absorption is 30 %. Therefore, for 1 kg of hydrogen storage, required volume of Mg based metal hydride is only 22 litre and is also safer then gaseous storage. The volumetric comparison of gaseous storage at 150 kg/cm^2, low temperature (V based) and Mg based metal hydride for 1 kg H_2 are shown in Fig. 6.1.

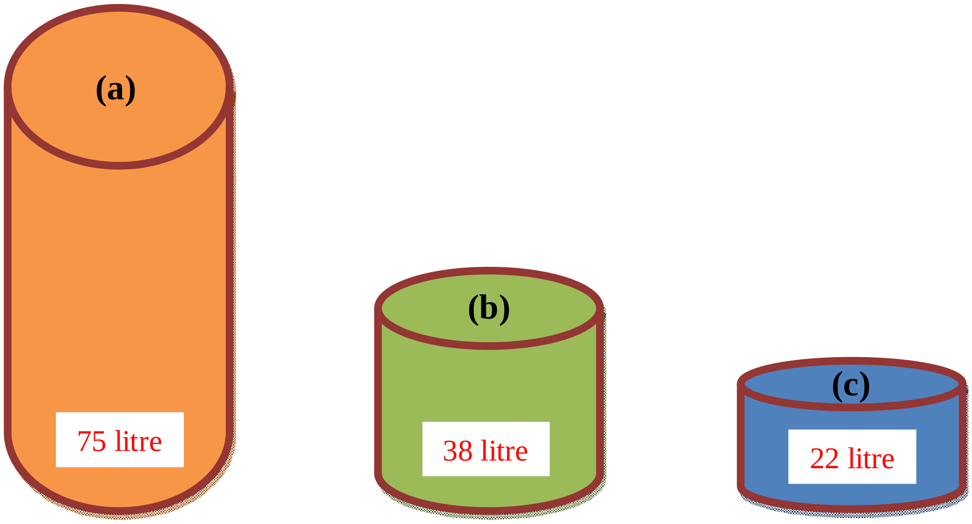

Fig. 6.1: Volumetric comparison of various hydrogen storage media gaseous for 1 kg H_2: (a) Gaseous storage at 150 kg/cm^2, (b) Low temperature based metal hydride and (c) Mg based metal hydride

6.3 Fuel Storage Applications

6.3.1 Stationary Fuel Storage

The weight requirements for stationary storage systems are not as severe as in mobile applications. Thus, it is likely that metal hydrides will be used at an earlier date for stationary storage [7]. Furthermore, the major fraction of the energy involved in operating a storage system incorporating this material can be supplied from waste heat (from a combustion device or fuel cell). The amount of high-grade energy (electrical) required to operate the metal-hydride storage system is small in comparison to the energy required for liquefaction or high pressure gas storage. The primary problem involved in the design of a hydrogen storage system based on the use of metal hydride is the problem of heat removal during charging and heat addition during discharge of the hydrogen. Three modes of heat transfer can be considered.

In ***fluid bed processing,*** hydrogen would be fluidizing gas used to move granular metal hydride powder bed from large storage tanks to small external hydriding or dehydriding units. The capacity of the system would be determined by the size of the storage tank and the rate of hydrogen release (kinetics) determined by the external process capacity and rate of heat addition.

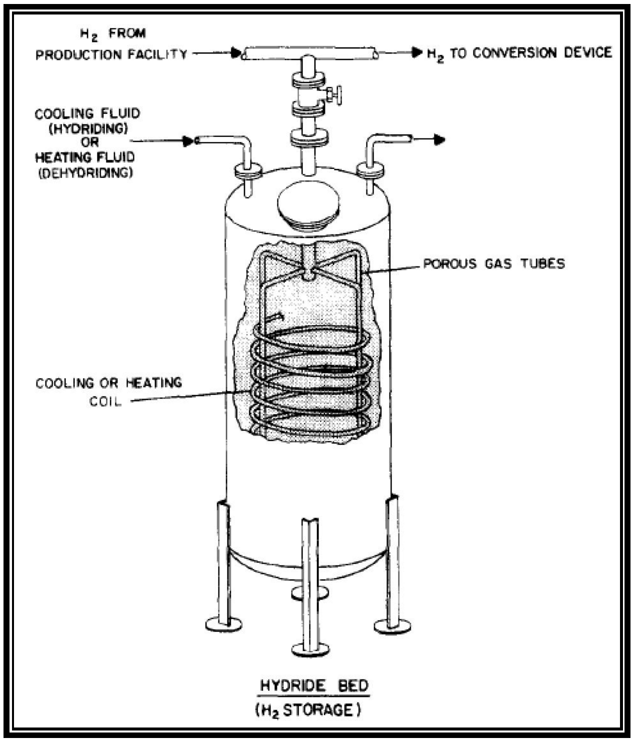

Fig. 6.2: Fixed metal hydride bed for hydrogen storage

In ***fixed bed internal heat exchange,*** the capacity and kinetic (heat transfer) functions are combined in one vessel [8, 9]. Fig. 6.2 shows the basic concept of "fixed-bed internal heat exchange". The basic storage module is a shell and tube heat exchanger. Granular metal hydride powder is contained on the shell side and heat is added and removed through tubes spaced throughout the bed of granular alloy. The bed contains an inlet/outlet header, connected to porous metal tubes also dispersed in the granular metal storage medium. This arrangement allows hydrogen to be added and removed without movement of the bed material. Thus, the two important design factors are the amount of heat transfer co-efficient and the effective thermal conductivity of the bed.

In ***fixed bed direct heat exchange*** configuration, a fixed bed of granular metal hydride powder is contained in a storage vessel [10]. Hydrogen is circulated through the bed and through an external heat exchanger by means of a circulating compressor. Heat produced by the reaction would be carried away from the fixed bed by the circulating process hydrogen stream and rejected in the external heat exchanger. The rate of heat addition would be controlled by the pressure and temperature of the circulating gas. The system would very likely be designed to operate at a constant optimal pressure and the rate of charging would be limited by the rate of heat rejection in the external heat exchanger.

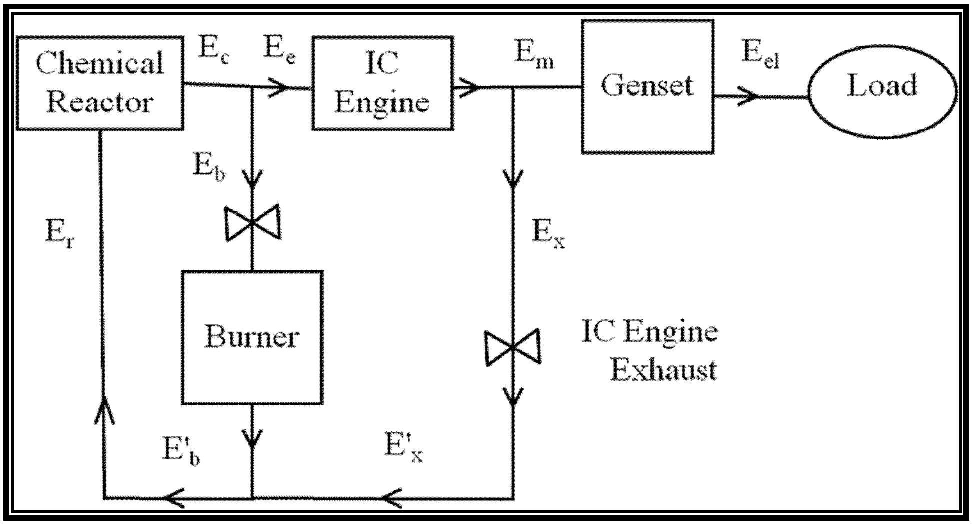

Fig. 6.3: Schematic diagram of the power system application of Mg based metal hydride

Fig. 6.3 shows a schematic illustration of the power system application of metal hydride. Such a system, involving the hydrogen storage concept is described the important application in electric utility systems. However, there remain a significant number of research and development problems to be solved, before the concept is economically viable.

In Fig. 6.3, E_c indicates the energy per mole of hydrogen, which is stored in the Mg based alloy compositions. E_b and E_e are energy diverted to burner and energy input to IC engine per one mole output from hydriding / dehydriding reactor, respectively. E_r indicates the energy required to liberate one mole of hydrogen from reactor. E_X and E_m indicate the energy of exhaust and mechanical energy input to genset per one mole output from hydriding / dehydriding reactor, respectively. Finally, E_{el} indicates the electrical energy to load per one mole liberated from reactor. Now, the efficiency of the electric storage system is computed using energy conversation principle, by the following basic equations:

$$E_c = E_e + E_b = 240 \text{ kJ/mole of } H_2 \qquad \text{---------------------} (6.2)$$

$$E_X = (0.65 \times 0.40) \times E_e \qquad \text{---------------------} (6.3)$$

$$E_r = \frac{75}{\eta_{HeatExchange}} = \frac{75}{0.80} = 94 \text{ kJ/ mole of } H_2 \qquad \text{---------------------} (6.4)$$

$$\therefore \quad E_r = (\eta_{\text{Burner}} \times E_b) + [(0.65 \text{ x } 0.40) \times E_e] = 94 \text{ kJ/ mole of } H_2$$

$$\therefore \quad 0.80 \times E_b + 0.26 \times E_e = 94 \text{ kJ/ mole of } H_2 \qquad \text{---------------------} (6.5)$$

Now, substituting for E_e in Eq. (6.2) by Eq. (6.5),

$$E_c = \frac{94 - 0.80 \times E_b}{0.26} + E_b = 240 \qquad \text{---------------------} (6.6)$$

$$E_b = \frac{240 - 361.5}{-2.07} = 58.7 \text{ kJ/mole of } H_2$$

$$\therefore \quad Ee \cong 240 - 58.7 \cong 181 \text{ kJ/ mole of } H_2$$

And, $E_{el} = 0.35 \times E_e = 0.35 \times 181 = 63.5$ kJ/ mole of H_2

Therefore, run efficiency of system is,

$$\eta_S = \frac{63.5}{240} = 0.265$$

$$\therefore \quad \eta_S \cong 27\ \%$$

Therefore, the Mg based alloy compositions may be used in such electrical energy storage system with system having 27 % efficiency.

6.3.2 Vehicular Fuel Storage

The developed metal hydrides have promise for specific motor vehicle applications. But, they can not be used to replace gasoline as an automotive fuel without compromising the conventional auto in terms of weight, cost, or complexity. In general, the effort of a vehicle fuel storage system is included a survey of potential hydride materials, an experimental investigation of the most promising candidates and the preparation of a reference design [7]. The use of a hydride in an automotive system for hydrogen storage is a considerable departure from conventional fuel storage systems. The uptake of hydrogen to form a hydride in the fuel tank involves an exothermic reaction and heat must be removed. Heat must be supplied to release fuel (as hydrogen) to the engine. The combustion of hydrogen in the internal combustion engine is subject to operational considerations not found with conventional fuels. A reference design demonstrates to a large extent the performance capability, in terms of range, speed, response, etc. of the system; and in the course of its development indicates research and development directions for the improvement of hydride materials and component designs.

Preliminary vehicle system studies are made using as a basis two hydrides, whose properties are relatively well known [11]. They are served to demonstrate and compare systems based on first, a lightweight, high-equilibrium temperature hydride with a relatively high heat of decomposition (such as Magnesium hydride); and second, Iron – Titanium hydride, which has a low equilibrium decomposition temperature and a low heat of reaction. The basic schematics diagram is shown in Fig. 6.4. For a hydride such as Magnesium hydride, a high temperature source of heat is necessary to release the hydrogen. Exhaust heat will have to be supplemented by heat supplied from a hydrogen burner fuelled from the hydride bed. Approximately 13 % of the bed will be utilized for this purpose. A small reservoir of Iron – Titanium hydride, coupled to the main reservoir, would be required to store hydrogen for starting purposes. This starter would be refilled as soon as the main bed started to deliver hydrogen.

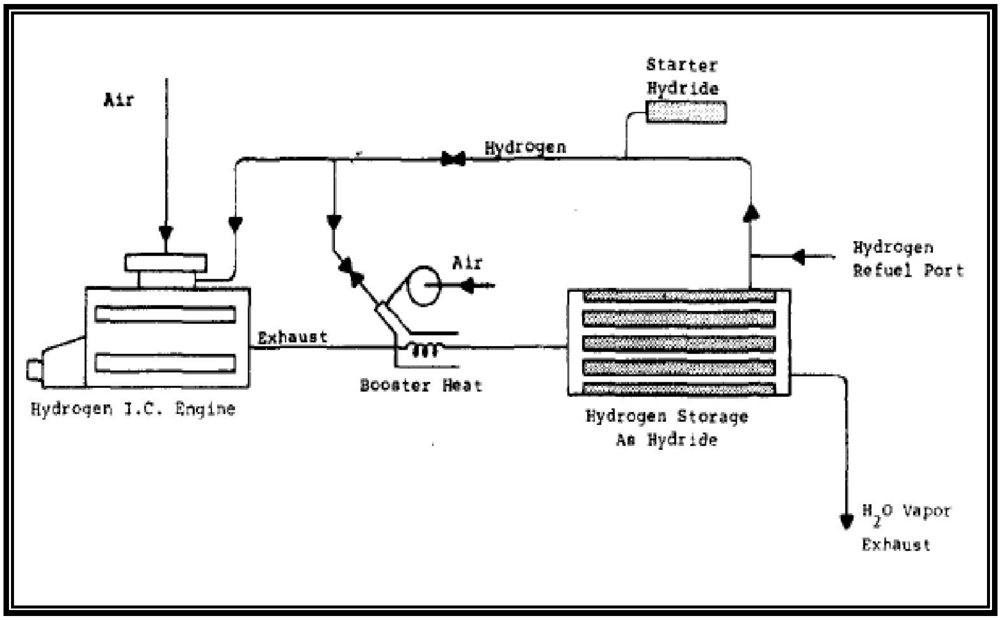

Fig.6.4: Application of hydride storage system to hydrogen fueled vehicles (supplemental heat case)

The use of a hydride with properties similar to the low temperature based hydrides would require minimal heating to release the hydrogen. The source of this heat could be either engine coolant, air preheated by heat from the coolant radiator, or heat from the exhaust. Hydrogen for start-up would be available on metal hydride bed (as a dead volume) [12]. This system is shown schematically in Fig. 6.5. A major emphasis in the reference design task is characterizing the behaviour of storage beds through the use of mathematical modelling techniques. Some general conclusions can be drawn from the modelling work. The rate of hydrogen release for the hydride is found to depend upon heat transfer rather than reaction rate. Future work should be devoted to this area of study as well as to the possibility of using hydrogen, stored as a hydride, as a supplemental fuel along with gasoline or methanol to provide run operation.

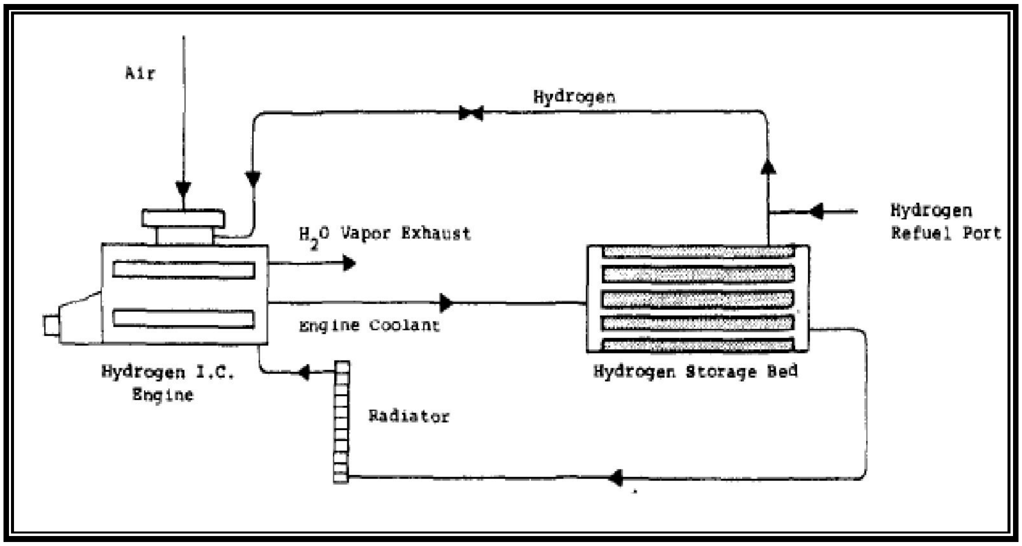

Fig.6.5: Application of hydride storage system to hydrogen fueled vehicles (non – supplemental heat case)

6.4 Electrical Energy Storage

6.4.1 Nickel Metal Hydride Battery (Electrodes)

Nickel metal hydride (NiMH) battery is an alternative to Ni–Cd battery [13]. The most common application of nickel metal hydride battery is heavy power requirement, portable electronic equipment and vehicular application. The design of NiMH batteries is almost identical to Ni–Cd except that a hydrogen absorbing negative electrode is used instead of a cadmium electrode. Generally, hydrogen absorbing electrode used is made out of AB_5 and AB_2 types metal hydrides [14, 15]. Nickel Oxyhydroxide (NiOOH) is the active material in the positive electrode. The negative electrode (hydrogen in the form of a metal hydride) is capable of a reversible absorbing / desorbing reaction during charging and discharging. An alkaline solution of diluted potassium hydroxide is used as an electrolyte. In a sealed design, most of the electrolyte liquid is absorbed by the separator and electrodes. The separator is usually a nylon blend material. The basic electro – chemical reaction is described as follows [16]:

Electro–chemical reaction:

Anode:

$$Ni(OH)_{2(s)} + OH^{-}_{(aq)} \longleftrightarrow NiO(OH)_{(s)} + H_2O_{(l)} + e^{-} \text{ --------------------- } (6.7)$$

Cathode:

$$H_2O_{(l)} + M_{(s)} + e^{-} \longleftrightarrow OH^{-}_{(aq)} + MH_{(s)} \qquad \text{--------------------- } (6.8)$$

The chemical process of NiMH battery is exothermic meaning that heat is given off during the charging process. When a NiMH cell reaches full charge the majority of the charging current is converted to heat and the cell temperature and pressure increase rapidly. NiMH batteries can operate effectively for over 500 cycles.

6.4.2 Fuel Cell

Metal Hydride Fuel Cell incorporates metal hydrides into the fuel cell hydrogen electrode, where it serves both as an anodic catalyst and as a hydrogen storage medium [17]. The metal hydride imparts charge storage to the hydrogen fuel cell electrode providing with a unique intrinsic energy storage capability. The anode contains metal hydride as the anodic catalyst together with carbon and PTFE materials with a nickel screen as a current collector [18]. The cathode contains metal oxides as the cathodic catalysts with carbon and graphite materials again with a nickel screen as a current collector. Potassium hydroxide is used as an electrolyte.

6.5 Thermodynamic Devices

Enthalpy changes during hydriding / dehydriding reactions are from ± 30 to ± 75 kJ per mole of H_2. The enthalpy value is changed slightly depending on the H° concentration in metal lattice. The average value of enthalpy formation for a specific metal hydride can be obtained from Van’t Hoff plots. The heats of exothermic and endothermic reactions can be used in thermodynamic devices such as heat pumps, refrigerators and compressors, when the reactions are cycled between the coupled reactor systems [19].

6.5.1 Heat Pump

Heat pump works on the principles of the thermodynamics based on the reversed "Carnot principle". This is illustrated in Fig. 6.6. The cyclic operation can be achieved by preparing two sets of coupled heat exchanger systems. In a coupled heat exchanger system, two metal hydrides with different hydriding / dehydriding P–C–T relations are chosen [20]. In each set, hydrogen is transferred between the coupled heat exchanger system in a back and forth manner. The hydrogen flow is switched to the opposite direction between a coupled heat exchanger systems periodically, after, a certain amount of hydrogen has been transferred from one side to the other.

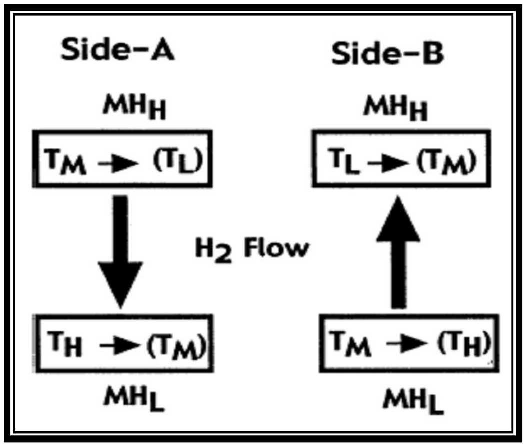

Fig. 6.6: Basic concept of a heat pump

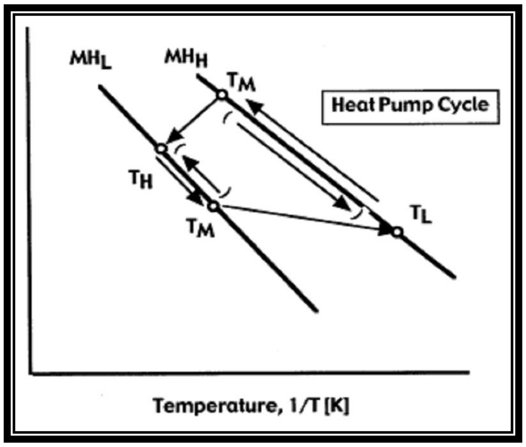

Fig. 6.7: Principles of a heat pump cycle (Van't Hoff plots on P–T relations)

The cyclic system is composed of two sets of coupled heat exchangers, which are operated periodically in a batch-wise manner. This can be understood as a type of the reversed Carnot cycle that generates heats as a heat pump and extracts heat from a closed space to the surroundings. The thermal energy sources are of three different temperature levels: (i) T_H as heat source or heat to be generated, (ii) T_M as heat source or sink, or (iii) T_L as low temperature source to be generated or heat sink. Any heat source (waste heat, solar thermal energy, or low-pressure steams) is used as the heat source at T_M. The heat pump cycle is illustrated in Fig. 6.7 [21]. In this, ambient air is applied as the heat sink at T_L. The thermal energy at T_M is upgraded to T_H by the exothermic reaction, when hydrogen is transferred between a coupled heat exchanger systems. The cyclic direction is anticlockwise in the heat pump cycle.

6.5.2 Refrigerator

Basic concept of a refrigerator is shown in Fig. 6.8 [22]. The hydrogen flows are periodically switched back and forth both in side A and side B in order to maintain the cyclic operation. In a refrigeration cycle, hydrogen is transferred in a clockwise manner, where T_H (waste heat, solar heat) is used as the heat source to release heat at T_M (ambient air, water), before and after generating low temperature source at T_L (refrigeration, air conditioning) (see Fig. 6.9) [23].

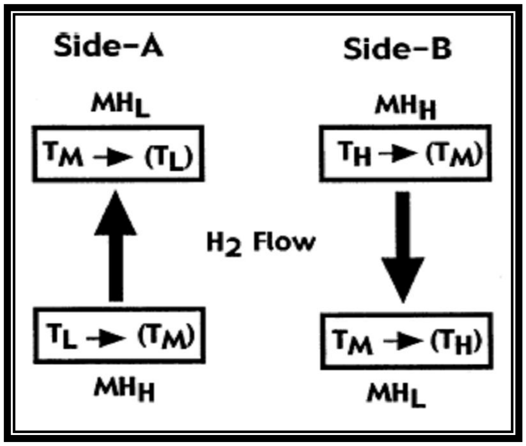

Fig. 6.8: Basic concept of a refrigerator

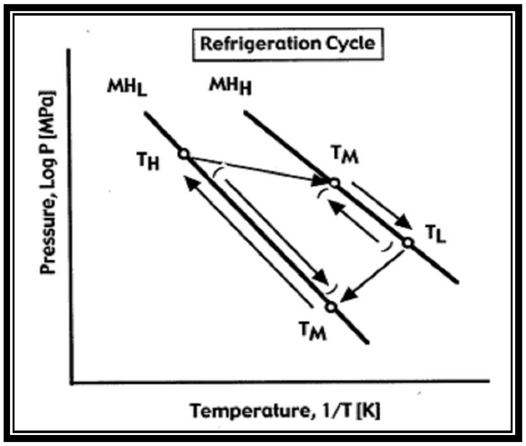

Fig. 6.9: Principles of refrigeration cycle (Van't Hoff plots on P–T relations)

Heat exchangers, where the *exothermic* reaction proceeds, act as the hydrogen acceptor and conversely, heat exchangers where the *endothermic* reaction proceeds, act as the hydrogen donor. The pressure level of hydrogen acceptor must be lower than that of hydrogen donor as the pressure difference is the driving force of hydrogen transfer. The driving force of any cyclic devices is the pressure difference in a coupled heat exchanger system with one in the high-pressure side and another in the low-pressure side. The pressure difference is largely dependent on (i) rate of hydrogen transfer, (ii) dynamic P–C–T behaviors of a coupled metal hydride system, and (iii) heat transfer characteristics of heat exchangers. Accordingly, it is not possible to design such devices without knowing the above listed factors that are only available by the collected experimental data.

6.5.3 Compressor

The pure hydrogen gas can be easily compressed by applying a thermodynamic cycle, if there are the enough heat sources available [24]. The maximum pressure attained by the compression is dependent on the P – T relation of a hydrogen-metal hydride system and is limited by the critical point of the selected system. However, it should be noted that the amount of high-pressure hydrogen is significantly dependent on the dynamic P–C–T relations. Also, these are influenced by the overall metal hydride characteristics and pressure vessel; like (i) amount of hydrogen-absorbing material, (ii) switchable numbers of hydriding / dehydridng cycles per unit time, and (iii) heat transfer characteristics of pressure vessels. It is estimated that the installation and operating costs must be higher than the conventional compressors. The compression system is only available for the pure hydrogen gas, but not for the hydrogen gas with air, moisture, and other gases. No industrial application has been reported.

6.6 Others

6.6.1 Catalysts for Hydrogen Reduction

Monatomic hydrogen stored in the crystalline lattice exhibits strong reactivity against materials. That is in contrast with the surface or physically adsorbed at the surface of metal hydride particles both in gas–solid reactions ($H_2 \longleftrightarrow 2H^\circ$) and electrochemical reactions ($H^\circ \longleftrightarrow H^+ + e^-$). A typical example of such chemical reductions is the synthesis of pure methane from CO_2 adsorbed on the fluorinated metal hydride surface [25];

$$CO_2 + 8H^\circ \longleftrightarrow CH_4 + 2H_2O \qquad \text{---------------------} (6.9)$$

The reaction in Eqn. (6.9) proceeds under moderate temperature and pressure conditions periodically between hydriding and dehydriding processes. It had been developed on a pilot-plant scale for recovering CO_2 to synthesize methane (CH_4) as a fuel. In the process, the produced methane and steam easily leave the fluorinated metal hydride surface to be replaced with CO_2 molecules approaching consecutively to the fluorinated surface. No poisoning by the adsorbed CO_2 has been observed during a long-term operation.

6.6.2 Sensor Devices

The equilibrium pressure of metal hydrides varies as a function of protium (H°) concentration and temperature. As the pressure–temperature relation can be expressed by a straight line in a Van’t Hoff plot, the pressure changes as a function of temperature have been expected to be applicable for sensing devices [26]. These are temperature sensors, pressure actuators, and limiting switches. However, the pressure change is significantly dependent on the dynamic P–C–T relations that are influenced by the overall heat transmission characteristics of sensing devices; like, (i) packing density, (ii) thermal mass, (iii) thermal conductivity and (iv) wall thickness.

6.6.3 Purification

The metal hydride surface is easily poisoned and deactivated by contact with air, moisture, CO, NO_2, SO_2, H_2S, and other materials [27]. This is caused by the extreme reactivity of the activated surface of metal hydride powders. It should be remembered that the metal hydride surface reactive in the gas–solid system not only with hydrogen molecules, but also other materials. The only possibility for the separation and purification is to develop the surface that does not exhibit reactivity against impurities. Presently, no practical separation and purification process has been developed except the small laboratory devices.

REFERENCES

1. P. Dantzer, Metal Hydride Technology: A Critical Review, *Hydrogen in Metals III, H. WIPF, Ed., Springer, Berlin* (1997) 279–340.
2. A. Zuttel, A. Borgschulte and L. Schlapbach, Hydrogen as a future energy carrier, *WILEY–VCH Verlag GmbH & Co. KGaA* (2008) 127–129.
3. Robert C. Bowman Jr. and Gary Sandrock, Metal Hydrides for Energy Storage and Conversion Applications. http://trs-new.jpl.nasa.gov/dspace/bitstream/2014/7613/1/03-1636.pdf
4. G. Sandrock and R. C. Bowman, *J. Alloys and Compounds,* **356–357** (2003) 794–799.
5. V. Guther and A. Otto, *J. of Alloys and Compounds,* **293–295** (1999) 889–892.
6. D. Pukazhselvan, M. Sterlin Leo Hudson, B. K. Gupta, M. A. Shaz and O. N. Srivastava, *J. of Alloys and Compounds,* **439** (2007) 243–248
7. K. C. Hoffman, J. J. Reilly, F. J. Salzano, C. H. Waide, R. H. Wiswall and W. E. Winsche, *Int. J. of Hydrogen Energy,* **1** (1976) 133–151.
8. C. Z. Wu and C. T. Hsu, Metal hydride canister apparatus, (2005) *Patent No. US2005/0103196A1*.
9. J. Y. S. Yang and M. Kao, Metal hydride storage canister design and its manufacture, (2006) *Patent No. US6993888B2*.
10. R. L. Woolley, Apparatus and method for transferring heat to and from a bed of metal hydrides, (1980) *Patent No.US4185979*.
11. P. M. Golben, Metal hydride based vehicular exhaust cooler, (2005) *Patent No. US2005/0274493A1*.
12. D. B. Mackay, B. C. Nielson, D. L. Henriksen, R. E. Billings, H. M. Simons and P. P. Hindmarsh, Hydride Fuel System, (1977) *Patent No. 4016836*.
13. Nickel–Metal Hydride Batteries Handbook, *Panasonic* (1998) 7–11.
14. K. Young, C. Fierro, B. Reichman, M. A. Fetcenko, J. Koch and A. Zallen, Nickel metal hydride battery design, (2005) *Patent No. US2005/0238959A1*.
15. S. Ito and H. Sakamoto, Nickel metal hydride battery, (2008) *Patent No. US2008/0160408A1*.
16. http://en.wikipedia.org/wiki/Nickel-metal_hydride_battery
17. S. R. Ovshinsky and D. A. Corrigan, Metal hydride fuel cells, a new approach, *Fuel cell magazine* (2005) 25–28.

18. www.battcon.com/PapersFinal2005/Fokpaper2005.pdf
19. C. Park, K. J. Kim, J. Gottschlich and Q. Leland, High performance heat storage and dissipation technology, *Proceedings of ASME International Mechanical Engineering Congress & Exposition, Orlando, Florida*, November 5–11 (2005) 1 – 8.
20. S. Suda, Y. Komazaki, H. Narasaki, and M. Uchida, *J. of the Less Common Metals,* **172–174 (3)** (1991) 1092–1110.
21. H. Bjurstrom and S. Suda, *Int. J. of Hydrogen Energy,* **14 (1)** (1989) 19–28.
22. M. R. Ally, W. J. Rebello and M. J. Rosso, Metal hydride chemical heat pumps for industrial use, *Proceedings from the Sixth Annual Industrial Energy Technology Conference Volume II, Houston, TX*, April 15–18 (1984) 686 – 693.
23. S. Srinivasa Murthy, Metal hydride based cooling systems with hydrogen as working fluid, *1st European Conference on Polygeneration, Tarragona (Spain),* 16–17 October (2007) 199–215.
24. Z. Feng, B. Deyou, J. Lijun, Z. Liang, Y. Xiaoyu and Z. Yiming, J. *of Alloys and Compounds,* **231 (1–2)** (1995) 907–909.
25. S. Suda, K. Iwata, Y. M. Sun, Y. Komazaki and F. J. Liu, *J. of alloys and compounds,* **253–254** (1997) 668–672
26. P. M. Golben, Thermally activated metal hydride sensor / actuator, (1983) *Patent No. 4,377,209*.
27. X. L. Wang, K. Iwata and S. Suda, *J. of Alloys and Compounds,* **231 (1-2)** (1995) 860–864.