



Metal hydrides based high energy density thermal battery



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ABSTRACT

A concept of thermal battery based on advanced metal hydrides was studied for heating and cooling of cabins in electric vehicles. The system utilized a pair of thermodynamically matched metal hydrides as energy storage media. The pair of hydrides that was identified and developed was: (1) catalyzed MgH_2 as the high temperature hydride material, due to its high energy density and enhanced kinetics; and (2) $\text{TiV}_{0.62}\text{Mn}_{1.5}$ alloy as the matching low temperature hydride. Further, a proof-of-concept prototype was built and tested, demonstrating the potential of the system as HVAC for transportation vehicles.

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1. Introduction

Thermal energy storage (TES) is one of the most promising approaches for harnessing and utilizing thermal energies, such as solar energy and industrial waste heat. TES is generally classified by different forms of storing heat such as: sensible heat, latent heat, and chemical energy [1]. Of all these forms, the use of thermo-chemical energy has received growing interest due to its intrinsic high energy-density [2]. In particular, a metal hydride based TES system is very appealing due to the fact that many metals and alloys can combine with hydrogen to form metal hydrides under favorable temperature and hydrogen pressure conditions. The basic idea of using metal hydrides for thermal engineering applications was originated in the 1970's, when Libowitz [3,4] suggested that the hydrogenation and dehydrogenation reactions could be used for TES. It was recognized that the substantial heats of reaction associated with hydrogenation (exothermic) and dehydrogenation (endothermic) reactions can be utilized for various practical purposes such as thermal storage, heat pumps, and heating and cooling systems [5]. There is considerable renewed interest in the use of metal hydrides for TES, including reports by Ono et al. [6], Yonezu et al. [7], and a recent review by Muthukumar et al. [8].

A common thread of the past research reports on metal hydride based thermal applications has been that most, if not all, utilize intermetallic AB_5 and/or AB_2 alloys as hydride materials [8], which

offer the advantages of excellent kinetic behavior and cyclic stability. However intermetallic metal hydrides suffer drawbacks including: (1) high cost of the misch metals; and (2) low hydrogen capacity (typically less than 1.8 wt.% hydrogen capacity), and hence low energy density, particularly low gravimetric energy density. The cost and weight of the intermetallic alloys are considered a major limitation, impeding their application in electric vehicles.

Bogdanovic et al. [9–11] suggested that Mg-based hydride systems could be used for TES because these systems cover a wide temperature range from 250 °C to 550 °C and have high thermal energy density, up to 2257 kJ/kg. However, pure MgH_2 , is known to have poor kinetic rates for both the dehydrogenation and hydrogenation reactions. Fortunately, recent progresses on hydrogen storage materials have shown that several nano-catalyzed Mg materials [12–17] are capable of absorbing a significant amount of hydrogen at room temperature. These findings have paved the way to practical application of Mg-based hydrides.

In this paper, we introduce the concept of a high-energy-density thermal battery based on exploiting the differences between hydrogen equilibrium pressures of Mg-based hydrides and intermetallic alloys (from AB_2 , AB_5 or BCC families) at relevant temperatures. The present research focused on a specified on-board application to develop a novel heating, ventilation, and air conditioning (HVAC) system for electric vehicles (EV). However, the methodology of the thermal battery could be extended to a much broader range of applications, including other transportation vehicles such as long haul trucks, stationary HVAC, solar thermal energy storage systems, and waste heat recovery and storage systems.

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2. Concept

As shown in Fig. 1, the thermal battery utilizes a thermodynamically-coupled pair of metal hydrides: one of which is designated as the high temperature (HT) hydride because it will provide heat. The HT hydride has a low equilibrium pressure and can release heat (exothermic) when it absorbs hydrogen; and it decomposes only at moderately higher temperatures. The other hydride is designated as the low temperature (LT) hydride because it will provide cooling (endothermic) when it dehydrogenates. The LT hydride has higher equilibrium pressure than the HT hydride has, and when releasing hydrogen the LT hydride absorbs heat from its local environment.

2.1. Cooling and heating (discharge mode)

At the beginning of a cycle, the LT hydride is contained in a low temperature hydride bed (LT-HB) and is in a hydrogenated state, while the HT hydride material is placed in a high temperature hydride bed (HT-HB) and is in a dehydrogenated state (alloy). When the valve between the two beds is open, hydrogen will flow from the LT-HB to the HT-HB (see Fig. 1, left), because the equilibrium H_2 pressure of the LT hydride is higher than that of the HT hydride. The endothermic dehydrogenation in the LT-HB and exothermic hydrogenation in the HT-HB occur simultaneously.

2.2. Recharging mode

External heat (could be from electric heater or other thermal energy sources) will be used to heat the HT-HB causing it to dehydrogenate, as shown in Fig. 1 (right). The H_2 released from the HT-HB will flow back to the LT-HB to rehydrogenate, i.e. recharge the LT hydride material in the LT-HB. During recharging, the external energy (e.g. from an electric outlet) is in essence stored as thermal chemical energy in the hydride that will be release for service during discharging. The system is hence termed a “battery”, a term that implies the storage of energy that can be used when and where it is needed.

In reality, using metal hydrides for heating/cooling of a vehicle faces many material and engineering challenges. The metal hydrides selected for the system must meet the following requirements:

- Two hydrides must have complimentary thermodynamic properties that would enable the discharging and charging of the system at specified desired temperatures for a given application.
- The hydride must have fast kinetic rates during dehydrogenation as well as hydrogenation which is essential to provide heating or cooling when and where it is needed.
- The system must have good cyclic stability and durability.
- The hydride must have both gravimetric and volumetric high energy density to be viable to compete with other energy sources such as electric battery.

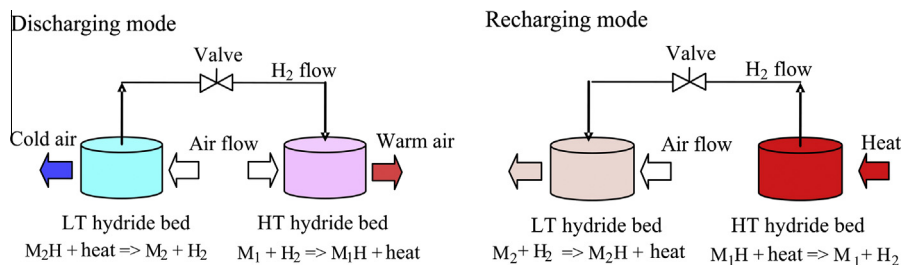


Fig. 1. Principle of the thermal battery based on metal hydrides.

3. Selection of the hydride materials

As mentioned above, the selection of the two hydride materials must have complimentary thermodynamic properties to enable discharging and charging of the thermal battery in desired temperature ranges. Specifically, for discharging of the thermal battery, the equilibrium pressure of the LT hydride must be high enough at the ambient temperature (e.g. -10 to 30 °C) so that the HT hydride metal can be hydrogenated at temperatures at or above the ambient temperature. For charging of the thermal battery, the equilibrium pressure of the HT hydride at an elevated temperature (e.g. 200 – 350 °C) must be high enough to hydrogenate the LT hydride metal at ambient temperature. To identify a candidate pair of hydride materials, a survey of a large number of potential hydride materials was conducted based on thermodynamics properties.

3.1. HT hydride

Fig. 2 is the van't Hoff plots of selected hydrides. The HT hydrides are on the left side of the diagram, while the LT hydrides are on the right. Fig. 2 shows that there are few options for the HT hydride considering that the temperature for recharging of the thermal battery should not be more than 400 °C for practical reasons. Catalyzed nano-sized MgH_2 was thus selected as the candidate HT hydride material. Because of a high usable hydrogen capacity, up to 7.0 wt.%, and a high reaction enthalpy of 75 kJ/mol H_2 , MgH_2 has a high gravimetric energy density. Relevant properties of MgH_2 and other comparable HT hydride candidates are summarized in Table 1. It can be seen that the gravimetric energy density and volumetric energy density of Mg/MgH_2 are 2831 kJ/kg and 4020 kJ/L, respectively.

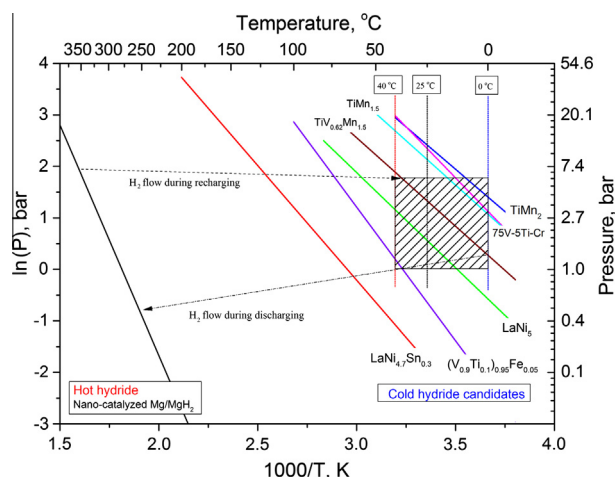


Fig. 2. Selection of a working pair of hydride materials based on van't Hoff plot.

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