INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–13

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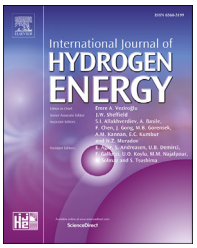

Numerical investigation of H_2 absorption in an adiabatic high-temperature metal hydride reactor based on thermochemical heat storage: MgH_2 and $Mg(OH)_2$ as reference materials

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ARTICLE INFO

Article history:
Received 21 March 2017
Received in revised form
10 May 2017
Accepted 18 May 2017
Available online xxx

Keywords:
Hydrogen storage
Thermochemical heat storage
Magnesium hydride
Magnesium hydroxide
Heat transfer
Numerical study

ABSTRACT

A two-dimensional mathematical model to predict the thermal performance of an adiabatic hydrogen storage system based on the combination of magnesium hydride and magnesium hydroxide materials has been developed. A simple geometry consisting of two coaxial cylinders filled with the hydrogen and thermochemical heat storage materials was considered. The main objective was to gain a better knowledge on the thermal interaction between the two storage media, and to determine the dependence of the hydrogen absorption time on the geometric characteristics of the reactor as well as the operation conditions and the thermophysical properties of the selected materials. The dimensions of the two compartments where the two materials are filled were chosen based on the results of a preliminary analytical study in order to compare the absorption times obtained analytically and numerically. The numerical results have shown that the hydrogen absorption process can be completed in a shorter interval of time than analytically as a result of the larger temperature gradient between the magnesium hydride and magnesium hydroxide beds. This was mainly due to variation of temperature in the thermochemical heat storage material during the more realistic dehydration reaction in the numerical solution. Larger temperature gradients, thus a faster hydrogen absorption process can also be achieved by increasing the hydrogen absorption pressure. Moreover, it was found that the increase of the thermal conductivity of the magnesium hydroxide material is crucial for a further improvement of the performance of the MgH_2–$Mg(OH)_2$ combination reactor.

Introduction

With the increasing awareness for economic and environmental concerns related to the use of fossil fuels, and the rising of the global energy demand, there has been an international commitment to make hydrogen the major energy carrier of the future. In this context, several hydrogen and fuel cell research and development programs have been conducted over the last decades [1], targeting first the

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http://dx.doi.org/10.1016/j.ijhydene.2017.05.123

Please cite this article in press as: Bhouri M, Bürger I, Numerical investigation of H_2 absorption in an adiabatic high-temperature metal hydride reactor based on thermochemical heat storage: MgH_2 and $Mg(OH)_2$ as reference materials, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.05.123

transportation sector [2,3], and extended thereafter to portable and stationary applications [2,4–6]. Among the encountered technical barriers, the development of a hydrogen storage system with high energy density has been identified as challenging [2]. Such a criterion is closely related to the choice of the hydrogen storage method, as well as the complexity of the hydrogen storage system design [7,8].

In case of large scale stationary applications, magnesium hydride-based hydrogen storage solution has been investigated due to the advantages in terms of energy density, cost, and safety [9–11], with the main focus on improving the energy efficiency of the studied system. Indeed, with an enthalpy of reaction of 75 kJ/mol H_2, a temperature above 300 °C is required to release hydrogen during the endothermic desorption process with an acceptable gravimetric hydrogen storage capacity of about 7 wt.%. Thus, in order to improve the energy efficiency of the system, the heat of reaction which corresponds to up to 31% of the lower heating value of hydrogen has to be exchanged with another system.

Delhomme et al. [10] investigated experimentally the thermal integration of a magnesium hydride (MgH_2) tank with a solid oxide fuel cell (SOFC) stack. In such an integrated system, the waste heat of the SOFC exhaust gases was recovered to provide the energy required for the endothermic desorption process. The heat exchange between the SOFC and the MgH_2 bed was ensured by the mean of a diathermic heat transfer fluid flowing through a finned heat exchanger inserted in the hydrogen storage system. The test of the experimental setup has enabled the identification of technical issues related to the coupling of the SOFC and the MgH_2 tank. Amongst others, it was found that it is necessary to optimize the heat exchanger design and ensure a better thermal insulation in order to achieve higher exchange efficiency between the two coupled systems. In subsequent studies [12,13], the same research group developed an adiabatic hydrogen storage system based on the combination of magnesium hydride and a phase change material (PCM). For such a reactor design, the heat of reaction to be extracted/produced during the hydrogen absorption/desorption processes corresponds to the latent heat of fusion/solidification of the PCM; and heat is conducted from one media to another due to the presence of a temperature gradient between the MgH_2 bed and the PCM. Such an operation principle had directed the choice of the PCM, so that its melting temperature should lay in-between the equilibrium temperatures of absorption and desorption. Besides, special attention was given to ensure that the PCM thermal conductivity does not impact the hydrogen absorption time. Based on these selection criteria, the metallic PCM, $Mg_{69}Zn_{28}Al_3$ with a melting enthalpy of 175 kJ/kg was used for the development of the MgH_2 tank.

Using the same PCM selected by Garrier et al. [13], Mellouli et al. [14] developed a two dimensional mathematical model to compare the performance of cylindrical and spherical configurations of a MgH_2–PCM reactor. Their numerical results showed that a shorter absorption time is achieved in the case of a spherical configuration, and emphasized the importance of optimizing the amount of used PCM as well as ensuring a perfect insulation of the MgH_2–PCM reactor. The same authors investigated numerically the performance of a Mg_2Ni/Mg_2NiH_4 system where the heat of reaction is stored in a phase change material composed of sodium nitrate, $NaNO_3$ [15,16]. Compared to the basic configuration where the Mg_2Ni alloy occupies the inner part of the tank, and is surrounded by an annular volume filled with the PCM, it was found that a better performance of the hydrogen storage system could be achieved if the PCM is also filled in cylindrical tubes distributed throughout the hydride bed [15], or if the hydrogen storage system is equipped with heat transfer fluid pipes [16].

Although the complexity of the MgH_2 tank was simplified with the use of PCM to store and recover the heat of reaction, the gravimetric capacity of the system was found to be 0.315 wt.% versus 6 wt.% for the MgH_2 + 5 wt.% ENG (expanded natural graphite) pellets incorporated into the storage tank, due to the weight of the PCM [13]. In a recent publication [17], the feasibility of an adiabatic MgH_2 reactor based on thermochemical heat storage has been discussed; and preliminary analytical results have shown that the combination of MgH_2 with magnesium hydroxide ($Mg(OH)_2$) can lead to a competitive hydrogen absorption time compared to the MgH_2–PCM reactor, while reducing the mass of the heat storage media by a factor of 4, using an inexpensive thermochemical heat storage material with a higher energy density compared to the metallic PCM, and operating at more flexible pressure and temperature conditions.

In this new reactor concept, the hydrogen storage media (MgH_2), and the thermochemical heat storage media $Mg(OH)_2$, are filled into two separated compartments of a thermally insulated container. During the uptake of hydrogen, the MgH_2 bed experiences an excessive temperature increase due to the exothermic nature of the H_2 absorption reaction. The released heat of reaction is conducted towards the $Mg(OH)_2$ bed which undergoes an endothermic reaction while storing the same amount of thermal energy, and releasing water vapor to an external water reservoir where the steam is, e.g., condensed. The opposite operation mode of the proposed system consists on the endothermic desorption of H_2. This occurs when the MgH_2 bed absorbs the heat of reaction released by the exothermic hydration reaction of magnesium oxide (MgO). In this case, the water vapor should be externally produced, and then supplied to the thermochemical heat storage media. The two described operating modes are governed by different conditions of temperature and pressure to be imposed to the hydrogen and thermochemical heat storage media as discussed in Ref. [17].

A similar concept has been presented in the case of a portable hydrogen generator patented by Long et al. [18]. The hydrogen generator includes a water supply and an adiabatic system containing a metal hydride (CaH_2), and a chemical hydride ($LiAlH_4$). Through the hydrolysis of CaH_2, hydrogen is generated and the released exothermic reaction heat is transferred to the $LiAlH_4$ media. Once this chemical hydride reaches a temperature above 100 °C, its reaction with the water vapor is initiated as well, and more hydrogen is generated, first through hydrolysis, and then through an endothermic decomposition promoted by the heat that is still available from the exothermic reaction of $LiAlH_4$ with water vapor.

Bürger et al. [19,20] studied an advanced reactor concept for complex hydrides. It is also based on the combination of a low temperature metal hydride ($LaNi_{4.3}Al_{0.4}Mn_{0.3}$) and a high

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