Numerical Simulation on Heat Transfer and Storage Performance of Hydrogen-Heat Storage Units

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Abstract

Hydrogen storage is an important part in the utilization of hydrogen energy. The combination of phase change materials and hydrogen solid storage system will effectively recover and utilize the reaction heat in the process of hydrogen absorption and desorption. This paper presents a hydrogen-heat storage unit consisting of metal hydride (MH) and phase change material (PCM). The performance of hydrogen ab/desorption and heat storage/release of MH-PCM units was studied by numerical simulation. To optimize the units structure and improve performance, the amount of PCM was discussed. The results show that the sensible heat storage ratio of PCM and the average desorption rate increases with the decrease of the amount of PCM.

Keywords: Hydrogen storage, Heat storage, Phase change material, Sensible and latent heat, Heat transfer

Nomenclature

Abbreviations		
Ca	reaction rate constant, s ⁻¹	
Cp	specific heat, J kg ⁻¹ K ⁻¹	
Ea	activation energy	
f	liquid fraction of PCM	
L	latent heat of PCM	
М	molecular weight, g mol ⁻¹	
Р	pressure, MPa	
R	universal gas constant, J K ⁻¹ mol ⁻¹	
Т	temperature, K	
wt	gravimetric hydrogen storage capacity	
x	reacted fraction	
ΔH	reaction enthalpy, J mol ⁻¹	
ΔS	reaction entropy, J mol-1 K ⁻¹	
Symbols		
ε	porosity	

λ	thermal conductivity, W m ⁻¹ K ⁻¹
μ	dynamic viscosity, Pa s
ρ	density kg m ⁻³

1. Introduction

As a high-quality secondary energy, hydrogen energy has become the potential direction of development in the future [1]. Safe and efficient hydrogen storage technology is an important foundation for commercialization. The main storage methods of hydrogen includes gas, liquid and solid storage. Among them, solid hydrogen storage has has been foucsed because of its strong safety, large hydrogen storage capacity, and purification of hydrogen.

Solid hydrogen storage materials, such as magnesium based alloys, have attracted much attention in recent years. Magnesium hydride (MgH₂) has a theoretical hydrogen storage capacity of 7.6wt%, which is considered as the most promising hydrogen carrier [2]. In recent years, researchers have done a lot of work to enhance the ab/desorption kinetics of the materials by producing an ultra-fine microstructure and intermixing catalytically active species [3,4]. However, the application of enhanced magnesium based alloys in hydrogen storage system still faces some key problems, such as the resistance of heat and mass transfer in the reaction process will significantly reduce the hydrogen capacity and reaction rate of the storage tanks [5]. At present, we can improve the effective thermal conductivity of the reaction bed by combining expanded graphite [6,7], metal foam [8,9] and other high thermal conductivity materials with hydrogen storage materials. For hydrogen storage system, heat and mass transfer of storage tanks can be enhanced by using various heat transfer structure [10-13], such as straight tube, spiral tube, finned, and microchannel heat exchanger. And numerical simulation has become the main research method [14].

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In recent years, a new method of using phase change materials (PCM) to recover and utilize reaction heat has been proposed to reduce energy consumption and simplify heat transfer structure [15-18]. Current research mainly focuses on the selection and physical properties of PCM in hydrogen storage systems. There is a lack of experience on how to desgin PCM and MH system, especially the discussion of the amount and the sensible/latent heat storage capacity of PCM have not been reported.

In this paper, we propose a new type of MH-PCM unit fitted cylindrical tanks for hydrogen storage and reaction heat storage at first. Then, a 2D mathematical model of heat and mass transfer within MH and PCM is detailed. Finally, the amount and the ratio of sensible and latent heat storage capacity of PCM on the performance of the units are discussed.

2. Mathematical model

In this study, we propose a new hydrogen-heat storage unit stacked inside a closed cylindrical tank as shown in Fig. 1a. The unit body consists of two types of layers. One is the MH layer pressed into a disc, which is composed of Mg and expanded graphite (ENG), the other is the PCM layer fixed by ENG adsorption or a metal container. The compact superposition of the three layers not only simplifies the structure of the hydrogen storage system, but also realizes the recovery and utilization of the reaction heat. A MH-PCM unit is



Fig. 1. Physical models: (a) hydrogen storage tank and MH-PCM unit, (b) simplification of MH-PCM units

used as a computational domain to understand the performance of the cylindrical tanks. To further save calculation time, A 2D axisymmetric model is adopted and the computational domain is shown in Fig. 1b. The following assumptions have been made [14,16,18]:

-The hydrogen pressure in the bed is uniform;

- -The local thermal equilibrium is valid;
- -Radiative heat transfer is neglected;
- -The thermophysical properties of are constant;
- -The convection of PCM can be neglected.

Considering these assumptions, the equations governing transfer and reactions in the MH-PCM units are as follows:

2.1 Governing equations for the MH bed

Chemical equilibrium of MH:

$$\ln \frac{p_{eq}}{p_0} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

Energy equation:

$$\rho \cdot c_{\rho} \cdot \frac{\partial T}{\partial t} + \varepsilon \cdot \rho_{g} \cdot c_{\rho g} \cdot \nabla (T \cdot \vec{V}_{r}) = \lambda \cdot \nabla^{2} T + S$$

where

$$\lambda = \varepsilon \cdot \lambda_g + (1 - \varepsilon) \cdot \rho_m C_{pm}$$
$$\rho \cdot c_p = \varepsilon \cdot \rho_g \cdot c_{pg} + (1 - \varepsilon) \cdot \rho_m \cdot c_{pm}$$

$$S = \frac{p_m \cdot w \cdot (1-\varepsilon)}{M} \cdot \frac{dx}{dt} \cdot \Delta H$$

Reaction kinetic equation [14]:

$$\frac{dx}{dt} = C_a \exp\left(-\frac{E_a}{R \cdot T}\right) \cdot \left(\frac{P_g}{P_{eq}} - 1\right) \cdot \frac{x - 1}{2\ln(1 - x)} \qquad P_g > 2P_{eq}$$
$$\frac{dx}{dt} = C_a \exp\left(-\frac{E_a}{R \cdot T}\right) \cdot \left(\frac{P_g}{P_{eq}} - 1\right) \cdot (1 - x) \qquad P_{eq} < P_g < 2P_{eq}$$
$$\frac{dx}{dt} = C_d \exp\left(-\frac{E_d}{R \cdot T}\right) \cdot \ln\left(\frac{P_{eq}}{P_g}\right) \cdot \frac{2x}{(-\ln x)^{0.5}} \qquad P_g < P_{eq}$$

2.2 Governing equations for the PCM

The energy equation of PCM based on the enthalpy formulation [18], as follows:

$$\frac{\partial H}{\partial t} = \nabla \cdot \left(\lambda_{pcm} \nabla(T) \right)$$

where: $H(T) = h(T) + \rho_{PCM} \cdot L_{pcm} \cdot f(T)$
 $h(T) = \int_{0}^{T} \rho_{pcm} \cdot C_{pcm} \cdot dT$

$$h(T) = \int_{T_{liq}}^{T} \rho_{PCM} c_{PPCM} dT$$

The liquid fraction based on volume can be defined as follows:

$$f = \begin{cases} 0 & T \leq T_{sol} \\ (T - T_{sol}) / (T_{liq} - T_{sol}) & T \geq T_{liq} \\ 1 & T_{sol} \leq T \leq T_{liq} \end{cases}$$

2.3 nitial and boundary conditions

2.3.1. Initial conditions

The MH temperature and pressure as well as the PCM temperature is solved based on the initial conditions:

ab:
$$T_{MH} = T_{PCM} = 573K$$
 $P_g = \begin{cases} P_0 + (P_{in} - P_0)t/10 & t < 10s \\ P_{in}, 1.0MPa & t \ge 10s \end{cases}$
de: $T_{MH} = T_{PCM} = T_{mpe}$ $P_g = 0.1MPa$

2.3 .2. Boundary conditions

The insulation boundary conditions of external surfaces: $\nabla T \cdot \vec{n} = 0$

The inter-phase boundary conditions in the MH-PCM:
$$\lambda_{MH} \cdot \nabla T_{MH} \cdot \vec{n} = \lambda_{PCM} \cdot \nabla T_{PCM} \cdot \vec{n} = 0$$

The symmetry boundary:

$$\nabla T_{pcm} \cdot \vec{n} = 0$$

2.4 Model validation

The above equations are solved by Fluent. The numerical simulation was compared with the experimental results of the mg-pcm system reported by Garrier et al[14]. The temperatures, hydrogen volume and ratio of MH bed during the adsorption and desorption process are shown in Fig. 2. The numerical results have a agreement with experimental data.



Fig.2. Comparison between experimental and simulation results: (a) Hydrogen desorption process: the initial temperature is 633 K, and hydrogen pressure is 0.1 MPa, (b) Hydrogen absorption process: the initial temperature is 573 K, and hydrogen pressure is 0.8 MPa.

3. Results and discussion

The thermophysical properties of the materials are listed in Table 1 [14,18].

Table 1 The thermophysica	I properties
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MH	PCM
ρ_m = 1800 kg/m ³	$ ho_{\it pcm}$ = 2260 kg/m ³
<i>c_{pm}</i> =1545 J/kg/K	с _{ppcm} =1820 J/kg/К
λ_m =2 W/m/K	λ_{pcm} =0.48 W/m/K
<i>E</i> =0.4	L _{pcm} =174000 J/kg
<i>wt</i> =0.05	<i>Т_{sol}</i> =580К
<i>∆H</i> =-75000 J/mol	<i>T_{lid}</i> =581K
∆S=-135.6 J/K/mol	H2
<i>E</i> _a =130 kJ/K/mol	<i>C_{pg}</i> =14000J/kg/K
<i>E</i> _d =41 kJ/K/mol	λ_g =0.24 W/m/K
<i>C</i> _a =10 ¹⁰ s ⁻¹	µ=8.9x10 ⁻⁶ Pa s
<i>C</i> _d =10 s ⁻¹	<i>M</i> =0.002kg/mol

3.1.The performance of MH-PCM units

Fig. 3a shows the temperature, MgH₂ conversion and liquid phase distribution in mh-pcm during hydrogen absorption. In the initial stage, the MH temperature reaches 644 K. At the inter-phase boundary of MH and PCM, the temperature of MH side decreases, and the reaction proceeded in a direction far from the boundary. With the increase of temperature at the PCM side, PCM melted away from the boundary. At 1000 s, the hydrogen absorption reaction was almost completed and PCM almost completely melted. But When the reaction is finished at 1074 s, there is still a large temperature difference between MH and PCM as Fig. 4a shown. Therefore, it will take time to balance the temperature between them. At 2500 s, the temperature of MH-PCM have been balanced and the equilibrium temperature (T_{mpe}) is 607 K.

The desorption process takes place at the initial temperature of T_{mpe} . As shown in Fig.3b, when hydrogen is released, the MH temperature reaches 558 K, which is the reaction equilibrium temperature at 0.1 MPa. As MH absorbing heat from PCM, the temperature of reaction bed increases gradually, and the temperature of PCM decreases away from the interphase boundary. In Fig.3b the desorption ratio of 99% is achieved at 4803 s, and finally the temperature of MH and PCM reaches equilibrium.







Fig.4. The temperature change at five monitoring points in the process of reaction: (a)absorption, (b)desorption

3.2. Effects of Phase Change Materials' amount

The amount of PCM is expresed by the thickness of layer(*d*). Fig.5 presents the effects of *d* on the ab/desorption time under the condition of complete hydrogen absorption(x=1). In the range of *d* from 24 mm to 18 mm, the hydrogen absorption time has little change. When the thickness is 17 mm, the time of hydrogen absorption increases obviously. This is because the temperature of MH is close to the reaction equilibrium temperature of 1.0 MPa in the later stage of reaction, which leads to the slow reaction rate. With the *d* decreased, the desorption time is reduced by 24% from 24 to 17 mm.



Fig.5. Effect of PCM thickness on (de)absorption time

3.3. The sensible and latent heat storage capacity

The effects of d on heat storage capacity are shown in Fig. 6. With the decrease of d, the latent heat storage capacity(Q_{lpcm}) of PCM decreases, while the sensible heat storage capacity(Q_{spcm}) increases. This is because Q_{lpcm} is proportional to mass, but Q_{spcm} is related to T_{mpe} - T_0 . In Fig. 5, T_{mpe} increased with the decrease of d, which results in the increase of Q_{spcm} . The total heat storage decreases slightly because the sensible heat of MH increases with the increase of T_{mpe} .



Fig.6. Effect of PCM thickness on heat storage capacity

4. Conclusions

MH-PCM units is proved to improve hydrogen ab/desorption performance with located heat storage/release. The thickness of PCM layer can be reduced to 17 mm under the condition of complete hydrogen absorption(x=1). With the decrease of PCM amount, the time of hydrogen absorption has small change when d>18 mm, and the time of hydrogen release decreases obviously. Because the amount of hydrogen absorption is constant, the heat storage capacity of PCM is almost unchanged, but the ratio of sensible heat storage capacity to latent heat storage capacity is obviously increased.

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