

Performance Optimization of a PCM based Array Metal Hydride Hydrogen Storage Reactor

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ABSTRACT

Metal hydrides (MH) are promising solid hydrogen storage materials with significant reaction heat effect applied in reactors. Phase-change materials (PCM) have been used as thermal management media in the MH reactor. To further improve the performance of such reactors, this study proposed a novel PCM-based MH (MgH₂) reactor with array layouts, aiming to construct a heat transfer interface with a high specific surface area. A mathematical model was developed to describe the process of heat transfer and absorption reaction. The results showed that an increase in the number of array units significantly increased the heat transfer area and enhanced the heat transfer and hydrogen absorption rate. The array reactor with seven units had a 1.8 times increase in the absorption rate compared to the traditional reactor with only one array unit.

Keywords: metal hydrides, hydrogen storage, phase change materials, array reactor, heat transfer

NONMENCLATURE

Abbreviations

MH	Metal hydride
PCM	Phase change material

Symbols

C	reaction rate constant, s ⁻¹
c_p	specific heat, J/(kg·K)
E	activation energy, J/(mol·K)
f	liquid fraction of PCM
L	latent heat of PCM, J/kg
M	molecular weight, kg/mol
n	Number of array unit
P	pressure, MPa
R	universal gas constant, J/(mol·K)

T	temperature, K
wt	gravimetric storage capacity
x	reacted fraction
ΔH	reaction enthalpy, J/mol
ΔS	reaction entropy, J/(mol·K)
ε	porosity
λ	thermal conductivity, W/(m·K)
μ	dynamic viscosity, Pa·s
ρ	density, kg/m ³

Subscripts

0	initial
e	effective value
g	gas
liq	liquefaction
m	magnesium hydride
p	Phase change material
sol	solidification

1. INTRODUCTION

Hydrogen energy utilization is an important direction for the future development of clean energy. Safe and efficient hydrogen storage technologies are urgently required for large-scale hydrogen applications [1]. In addition to gas- and liquid-state storage methods, solid-state storage based on hydrogen storage materials has emerged as a promising technology owing to its advantages of high-volumetric storage capacity, safety, and stability [2].

As a kind of hydrogen storage materials, Metal hydrides (MH) have exhibited good reversible reaction performance. Mg/MgH₂ have become the focus of current research due to its low price and high hydrogen storage capacity [3]. Many studies have been conducted on enhancing the performance of MgH₂ materials, including the improvement of the absorption and

desorption reaction kinetics and cyclic stability performance by producing an ultra-fine microstructure [4] and intermixing catalytically active species [5]. Nonetheless, the application of enhanced materials in fixed-bed hydrogen storage reactors still faces thermal management issues owing to the significant thermal effects during the hydrogen absorption/desorption process [6].

To effectively discharge or charge the reaction heat during hydrogen absorption or desorption, MH reactors are usually equipped with heat exchangers using heat transfer fluid (HTF) for thermal management [7]. Previous studies have explored the application of various heat exchangers such as straight and finned tubes [8, 9], spiral tubes [10, 11], and mini-channel tubes [12, 13] in MH reactors. Nonetheless, high-performance heat exchangers make the reactor structure complex, and the system must be equipped with a circulating cooling and heating subsystem for the HTF, which complicates the hydrogen storage system. In addition, the poor energy consumption efficiency of the system results from the direct dissipation of reaction heat by the heat transfer fluid (HTF) during the absorption process.

Thus, to address this issue, Garrier et al. [14] proposed a novel method that utilizes phase change materials (PCM) for the thermal management of MH reactors, which simplified the structure of the hydrogen storage system and effectively transferred and recycled heat by the melting-solidification behaviour of PCM. Recent research has explored the structure [15, 16], PCM types, and thermophysical properties [17-20] of such reactors. Alqahtani et al. [15] increased the heat transfer area of a PCM-based MH reactor by designing a PCM double-layer sandwich structure, resulting in a reduction in the hydrogen absorption and desorption times by 81.5% and 73%, respectively, compared with a PCM single-layer surrounding structure. Our previous work discussed the impact of PCM parameters (such as the PCM amount, melting point, and latent heat) and obtained a calculation method for the precise dosage of the PCM for MH reactors [20].

To further optimize MH reactors and take advantage of the simple structure and reaction heat recovery of the PCM thermal management method, this study proposed a novel PCM-based array MH hydrogen storage reactor with the aim of constructing a high specific surface area for the heat exchange interface to further enhance the heat transfer and absorption performance. A comparative numerical analysis was

performed to evaluate the performance of the array reactor against traditional PCM-based MH reactors.

2. MATHEMATICAL MODEL

In the traditional PCM-based MH reactor (Fig. 1a), the PCM was surrounded by a cylindrical reactor, and the reaction heat was transferred between the PCM and MH through the side surface of the reactor. However, the limited heat transfer area limits the further development of the performance. Thus, this study proposed an array MH-PCM reactor (Fig. 1b) utilizing the high specific surface area of the array layout to further enhance heat transfer and reaction performance. Seven smaller diameter cylindrical reactor units is installed in a cylindrical groove filled with the PCM of NaNO_3 to construct an ultra-high heat transfer surface area between MH and PCM. Each reactor unit is filled with the powdered Mg/MgH_2 hydrogen storage material. The thermophysical properties of Mg/MgH_2 , NaNO_3 , and H_2 are showed in Table 1 [19, 21].

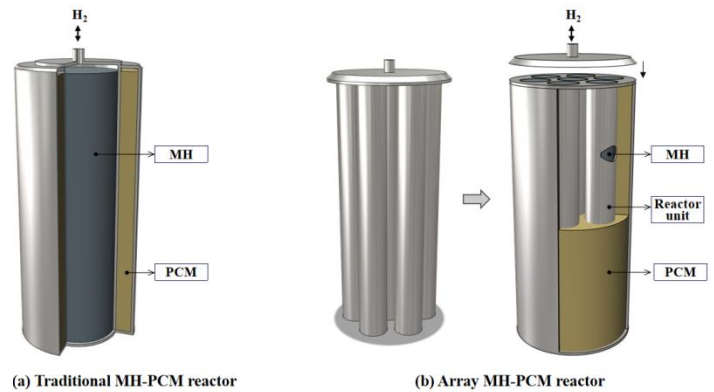


Fig. 1. The PCM based MH reactors with a (a) traditional layout and (b) novel array layout

The above reactors are standard cylinders, assuming that their top and bottom are adiabatic. Their calculation domains can be simplified to a two-dimensional circular region of the vertical views (Fig. 2) because of the periodicity of the reactor in the axial direction, which includes the MH and PCM zones (ignoring the wall thickness).

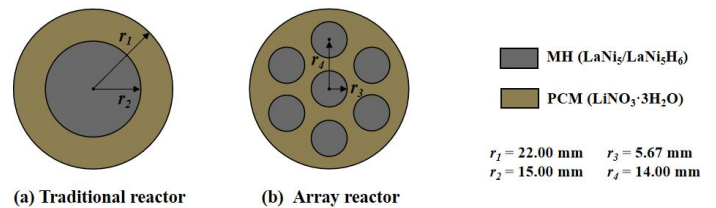


Fig. 2. The computational domains and dimensions of (a) traditional and (b) novel array MH-PCM reactors

Table 1. Reaction and physical parameters of MH, PCM, and H₂ [19, 21]

MH (Mg/MgH ₂)	PCM (NaNO ₃)	H ₂
$\rho_m = 1800 \text{ kg/m}^3$	$\rho_p = 2260 \text{ kg/m}^3$	$c_{p,g} = 14000 \text{ J/(kg}\cdot\text{K)}$
$c_{p,m} = 1545 \text{ J/(kg}^{-1}\cdot\text{K)}$	$c_{p,p} = 1820 \text{ J/(kg}\cdot\text{K)}$	$\lambda_g = 0.24 \text{ W/(m}\cdot\text{K)}$
$\lambda_m = 1.16 \text{ W/(m}\cdot\text{K)}$	$\lambda_p = 0.48 \text{ W/(m}\cdot\text{K)}$	$\mu_g = 8.9 \times 10^{-6} \text{ Pa}\cdot\text{s}$
$\varepsilon = 0.74$	$L = 174000 \text{ J/kg}$	$M = 0.002 \text{ kg/mol}$
$E_a = 130 \text{ kJ/(K}\cdot\text{mol)}$	$T_{sol} = 580.0 \text{ K}$	
$wt = 0.06$	$T_{lid} = 581.0 \text{ K}$	
$\Delta H = -75 \text{ kJ/mol}$		
$\Delta S = -135.6 \text{ J/(K}\cdot\text{mol)}$		
$C_a = 10^{10} \text{ s}^{-1}$		

To establish a mathematical model for the hydrogen absorption and heat transfer processes of MH-PCM reactors, the following assumptions were considered:

- The porous MH zone possesses local gas-solid thermal equilibrium.
- The reactor has ideal thermal insulation.
- The hydrogen pressure distribution in the reactor is uniform, and its natural convection can be ignored.
- The thermophysical properties of the materials are constant.
- The MH zone's volume expansion is disregarded.

The transfer and absorption processes are described by the equations governed in the following sections.

2.1 Governing equations

For MH zones, the reaction equilibrium temperature-pressure are determined by the Van't Hoff equation [10]:

$$\ln \frac{P_{eq}}{P_0} = \frac{\Delta H}{RT_m} - \frac{\Delta S}{R} \quad \text{where } P_0 = 0.1 \text{ MPa} \quad (1)$$

Energy equation of MH beds [12]:

$$\rho \cdot c_p \cdot \frac{\partial T_m}{\partial t} + \rho_g \cdot c_{p,g} \cdot \nabla(T_m \cdot \vec{V}_r) = \lambda_e \cdot \nabla^2 T_m + S \quad (2)$$

Where

$$\lambda_e = \varepsilon \cdot \lambda_g + (1 - \varepsilon) \cdot \lambda_m \quad (3)$$

$$\rho \cdot c_p = \varepsilon \cdot \rho_g \cdot c_{p,g} + (1 - \varepsilon) \cdot \rho_m \cdot c_m \quad (4)$$

$$S = \frac{\rho_m \cdot wt \cdot (1 - \varepsilon)}{M} \cdot \frac{dx}{dt} \cdot \Delta H \quad (5)$$

Reaction kinetic equations for hydrogen absorption process is expressed by Chaise et al [21].

$$\frac{dx}{dt} = C \exp\left(-\frac{E}{R \cdot T_m}\right) \cdot \left(\frac{P_g}{P_{eq}} - 1\right) \cdot \frac{x - 1}{2 \ln(1 - x)} \quad (6)$$

For PCM zones, the energy equation based on the enthalpy formulation are as follows [20]:

$$\frac{\partial H}{\partial t} = \nabla \cdot (\lambda_p \nabla(T_p)) \quad (7)$$

Where H is the sum of sensible heat:

$$H(T_p) = \int_{T_{liq}}^{T_p} \rho_p c_{p,p} dT_p + \rho_p \cdot L \cdot f(T_p) \quad (8)$$

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

$$f = \begin{cases} 0 & T_p \leq T_{sol} \\ (T_p - T_{sol}) / (T_{liq} - T_{sol}) & T_{sol} \leq T_p \leq T_{liq} \\ 1 & T_p \geq T_{liq} \end{cases} \quad (9)$$

2.2 Initial and boundary conditions

The initial temperature of MH and PCM is 573 K. The hydrogen absorption pressure is 1.0 MPa.

The adiabatic boundary condition is as follows:

$$\nabla T \cdot \vec{n} = 0 \quad (10)$$

The MH-PCM heat transfer boundary is as follows:

$$\lambda \frac{\partial T}{\partial \vec{n}} = h_f \Delta T \quad (11)$$

3. MODEL VALIDATION

The governing equations mentioned above were solved by Fluent 14.5, with user-defined functions used to interpret the equation of internal heat source and reaction kinetics. The zones of MH and PCM were discretized into quadrilateral grids for solving the equations. To validate this model, the simulation and experimental results were compared. In the experimental study of Garrier et al. [14], a reactor filled with Mg/MgH₂ compacted disks was surrounded by the PCM of Mg₆₉Zn₂₈Al₃. From the comparison results of the temperature at a point on the MH bed and the hydrogen absorbed volume during the absorption process, the simulation results have a good agreement with the experimental data. Thus, the numerical model is valid for this study.

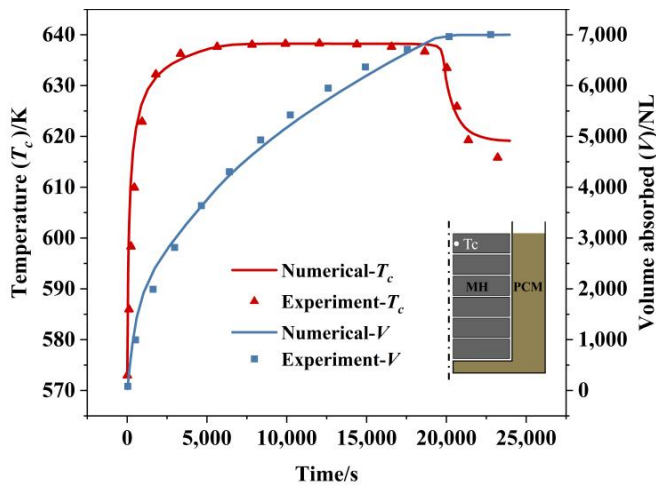


Fig. 3. Comparison of the simulation and experimental results for the PCM based MH reactor

4. RESULTS AND DISCUSSION

4.1 Comparison of two reactors

As shown in Fig. 4a, in the initial absorption stage, the temperature of the MH zone increased rapidly and approached the calculated reaction equilibrium temperature of 644 K (Van't Hoff equation) at 1.0 MPa. The released absorption heat was transferred from the MH to the PCM, causing the temperature of the MH to gradually decrease, and the PCM to absorb the heat and melt (Fig.4b). The PCM effectively transferred and absorbed the reaction heat during the absorption process. Subsequently, the temperatures of the MH and PCM gradually approached equilibrium, signifying the completion of the hydrogen absorption reaction.

The MH-PCM reactor with an array layout has a lower peak temperature in the initial absorption stage compared to the reactor with a traditional layout. (Fig.

4a), and the cooling rate of the MH bed was faster. More importantly, the excellent heat transfer performance accelerated the absorption rate. As shown in Fig. 4b, the absorption completion times of the array and traditional reactors were 1,157 and 3,269 s, respectively, and the array reactor achieved an approximate 1.8 time increase of average absorption rate.

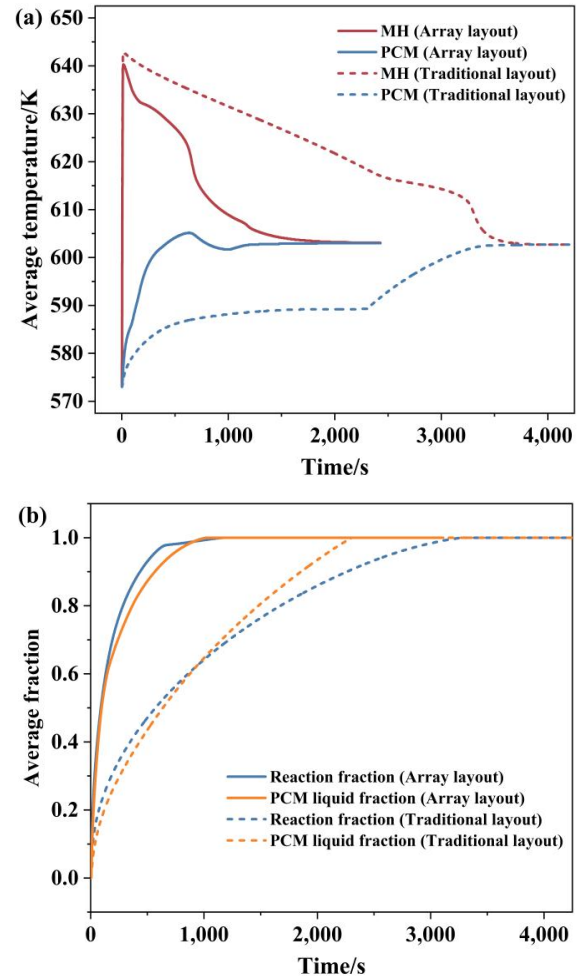


Fig. 4. Comparison of (a) average temperatures and (b) reaction/liquid-PCM fractions of hydrogen absorption in two types of MH-PCM reactors

4.2 Number of array units

For the array MH-PCM reactor, the number of array units (n) determined the size of the heat-transfer area between the MH and PCM zones. When $n = 1$, the reactor had a traditional layout. Fig. 5 showed the top view of the array reactors with unit numbers of 3, 5, 7, and 9, where the MH zones are uniformly distributed in the PCM zone and the area or volume of the MH and PCM zones remain constant. As shown in Fig. 6a, when n increased from 3 to 9, the MH cooling and PCM

heating rates significantly accelerated during the absorption process after the MH temperature reaching its maximum values. Correspondingly, in Fig. 6b, the absorption completion time decreased from 1,720 s at $n = 3$ to 915 s at $n = 9$, and the average rate of hydrogen absorption exhibited a 88.0% increase. But, when n increased from 7 to 9, the heat transfer and reaction enhancement effect is significantly reduced. This phenomenon could be attributed to the heat transfer resistance (low thermal conductivity) on the MH and PCM zones.

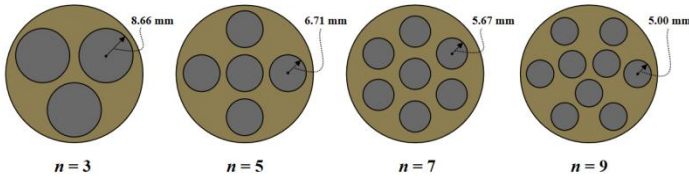


Fig. 5. Vertical views of array MH-PCM reactors with various array unit numbers (n)

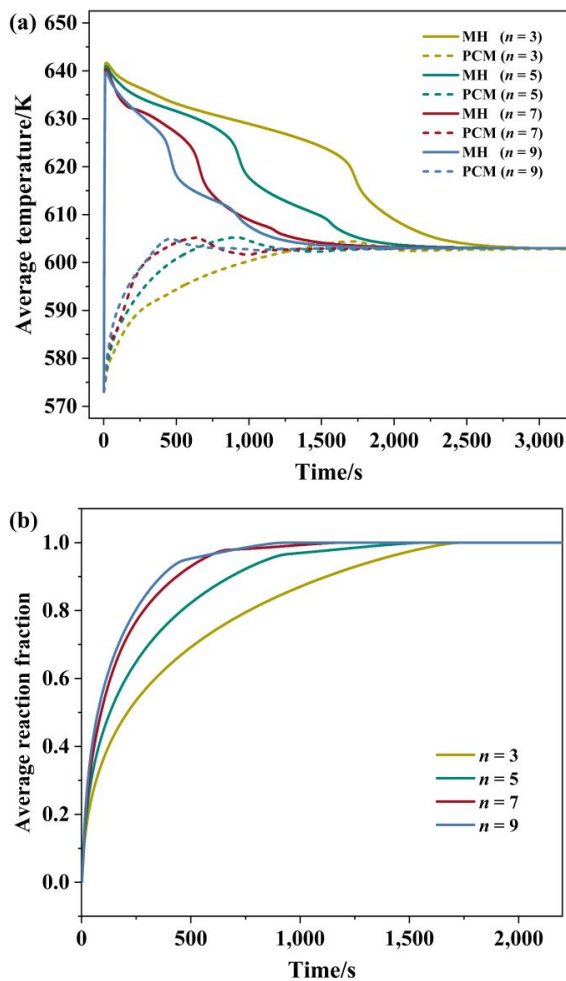


Fig. 6. (a) Average temperatures and (b) reaction fractions of array MH-PCM reactors with various numbers of array units during the absorption process

5. CONCLUSIONS

In this study, a novel PCM-based MH reactor with array layouts (array MH-PCM reactor) was developed to construct a high specific surface area for the heat transfer interface. A mathematical model was developed to describe the heat transfer and absorption reaction process. The comparison results showed the average hydrogen absorption rate of the array reactor (with seven array units) was 1.8 times that of the traditional reactor (with one array unit), owing to the significant enhancement of heat transfer performance by an increase in heat transfer area of 1.6 times. The increase in the number of array units can continuously increase the heat transfer area and accelerate heat transfer and reaction rate. The average rate of hydrogen absorption increased by 88.0% when the unit number increased from 3 to 9.

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DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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