

Operating Characteristics of Metal Hydride Hydrogen Storage with Pressure Regulation

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ABSTRACT

Hydrogen energy is an indispensable technology to achieve carbon neutrality in China. Currently, closed-loop hydrogen-related technology still faces great challenge in hydrogen storage. Metal hydride hydrogen storage (MHHS) is one of the promising forms in increasing hydrogen storage density and technical security. Whereas, MHHS technology involves complex physical-chemical issues in heat-mass transfer and absorption reaction. Based on a multi-field coupling model, the present work focuses on enhancing the running performance of MHHS by pressure regulation. It is found that with suitable pressure, the thermal load on reactor bed has been weakened effectively at the cost of an acceptable reduction of reaction rate. The T_{\max} of RB was reduced from 98°C to 75°C at the variable pressure operation mode. The present research provides a guidance with pressure regulating operation for MHHS technology.

Keywords: hydrogen storage, Metal hydride, heat-mass transfer, pressure regulation

NOMENCLATURE

Abbreviations

MH	Metal Hydride
MHHS	Metal Hydride Hydrogen Storage

HTF	Heat Transfer Fluid
RB	Reaction Bed
Nomenclature	
T_{\max}	Peak temperature of reactor bed (°C)
T_{ave}	Average temperature of reactor bed (°C)
p_{in}	Inlet pressure (MPa)
F	Hydrogen absorption fraction (-)
E_a	Reaction activation energy (J mol ⁻¹)
R_g	General gas constant (J mol ⁻¹ K ⁻¹)
P_{eq}	Equilibrium pressure (MPa)
K	Permeability (m ²)
λ_e	Effective thermal conductivity (W m ⁻¹ K ⁻¹)
S_m	Mass source term (kg m ⁻³ s ⁻¹)
S_t	Heat source term (W m ⁻³)
ρ_g	Density of hydrogen (kg·m ⁻³)
ΔH	Enthalpy of Reaction (J mol ⁻¹)
Greek Symbols	
ε	Porosity of MH bed (-)

1. INTRODUCTION

Hydrogen energy is one of the most promising options to reverse the rugged energy patterns and simultaneously build a low-carbon, sustainable and environmental-friendly world. Because of the vast reserves and free pollution, hydrogen has long been regarded as an alternative energy carrier and

storage medium^[1]. A complete hydrogen cycle system includes hydrogen preparation, storage, transportation, distribution and application. The major challenge in a large-scale application of hydrogen is how to store hydrogen safely and efficiently^[2]. Due to the high diffusion capacity and explosion of hydrogen, a proper solution of hydrogen energy storage and transportation has become a key issue in developing hydrogen energy^[3]. Traditional hydrogen storage technologies, such as high-pressure hydrogen storage and low-temperature liquefied hydrogen storage, are simple in structure, low in cost, and fast in charging and discharging hydrogen. However, the density of stored hydrogen is low, and the storage tank is relatively heavy. There are also some security risks, so this method is not suitable for large-scale hydrogen energy utilization. Although the low-temperature liquid technology has considerable hydrogen storage density, the cost is high. It is more suitable for the aerospace field^[4]. In contrast to conventional hydrogen storage technology, MHHS technology adopts metal compounds as hydrogen storage materials to absorb / desorb hydrogen in a reversible chemical reaction. The reaction is characterized by mild charging and discharging conditions, large hydrogen absorption, high safety, and excellent hydrogen absorption and desorption kinetics. It has a greater commercial value especially for vehicle-mounted energy storage systems^[5, 6]. Typical MH alloy systems includes LaNi₅ system^[7], MgNi system^[8], ZrCo system^[9], etc., among which La-Ni alloys are most widely investigated.

The MHHS still faces great challenges. On one hand, the absorption reaction requires suitable temperature and pressure to achieve the optimal absorption state. On the other hand, the reaction process is accompanied by heat release which will influence the reaction kinetics evolution. Therefore, an appropriate thermal management for the H₂ absorption reaction is of vital importance^[10, 11]. To address the thermal management of MH storage technology. H. Dhaou et al.^[12] designed MH

reactor with finned spiral heat exchanger. Yang et al.^[13] considered the dynamic matching of convective heat transfer and reaction kinetics during reactor operation. As the reaction proceeds, the reactor heat transfer capacity controls the reaction rate. Recently, Yang Ye et al.^[14] combined phase change heat storage materials with conventional jacketed heat transfer techniques. This method has a faster hydrogen absorption rate and heat transfer rate, which provides a new idea for thermal management of the reactor. Since MH technology is a multiple physical and chemical processes involving heat-mass transfer and chemical reactions. It is necessary to investigate its complex heat mass transfer and reaction coupling mechanism to optimize and improve the design of MHHS reactors. However, the dynamic characteristics and pressure regulation operation are not sufficiently studied. Therefore, this paper investigates the running characteristics and effects under varying pressure regulations. The coupled relation of hydrogen absorption evolution and temperature distribution of reaction bed (RB) has been discussed in detailed. In this paper, for the first time, the thermal management of RB is performed by regulating the pressure. Provides a guidance with pressure regulating operation for MHHS technology.

2. NUMERICAL MODELING

In this study, LaNi₅ alloy is used as an example. The chemisorption reaction between H₂ and LaNi₅ alloy occurs at a certain temperature and pressure, allowing hydrogen to enter the crystal voids and be sequestered. The cross-sectional structure of the cylindrical reactor is shown in Fig. 1. The RB is porous, and the cooling media flows to remove the reaction heat.

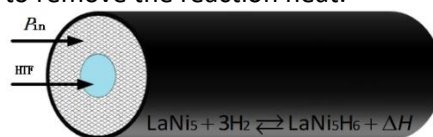


Fig. 1 Hydrogen storage reactor

2.1 Reaction kinetic equations

The equilibrium pressure of hydrogen absorption for MH is given by the Van't Hoff

equation^[15], and a modified equilibrium pressure P_{eq} model is used in this paper:

$$p_{eq} = \exp\left(13.1 - \frac{3.7 \times 10^3}{T}\right) + 0.038 \tan\left(\pi F - \frac{\pi}{2}\right) \quad (1)$$

The reaction rate is:

$$\frac{dF}{dt} = C_a \exp\left(-\frac{E_a}{R_g T}\right) \times \ln\left(\frac{p}{p_{eq}}\right) \times (1-F) \quad (2)$$

2.2 Mass transfer equation

The continuity equation for hydrogen flow through the porous RB is as follows:

$$\frac{\partial \varepsilon \rho_g}{\partial t} + \nabla \cdot (\rho_g \vec{V}_g) = -S_m \quad (3)$$

And the hydrogen is regarded as idea gas, \vec{V}_g is the Darcy velocity, and s_m is the hydrogen absorption mass source term, expressed as:

$$S_m = C_a \ln\left(\frac{p}{p_{eq,a}}\right) \exp\left(-\frac{E_a}{R_g T}\right) (1-F) \quad (4)$$

The mass equation is as below:

$$(1-\varepsilon) \frac{\partial \rho_s}{\partial t} = S_m \quad (5)$$

The momentum equation adopts Darcy's law as follows:

$$\vec{V}_g = -\frac{K}{\mu_g} \nabla p \quad (6)$$

Where K is the bed permeability, μ_g is the hydrogen viscosity coefficient.

2.3 Heat transfer equation

Assuming a local thermal equilibrium between the gas and the RB, the corresponding energy equation is as follows:

$$(\rho c_p)_e \frac{\partial T}{\partial t} + \rho_g c_{pg} \vec{V}_g \nabla T = \nabla \cdot (\lambda_e \nabla T) + S_T \quad (7)$$

where, $(\rho c_p)_e$ denotes the effective heat capacity, λ_e is the effective thermal conductivity. The source term S_T is obtained as follows:

$$S_T = S_m \left(\frac{\Delta H}{M_{H_2}} - T(c_p^g - c_p^s) \right) \quad (8)$$

In this paper, the initial reaction fraction is set to 0.1, and the boundary conditions are constant pressure inlet and constant temperature inlet. The relevant parameters are shown in Table 1.

Table 1 Parameter configuration

Parameters	Values
H ₂ heat capacity	14890 J kg ⁻¹ K ⁻¹
Metal heat capacity	419 J kg ⁻¹ K ⁻¹
H ₂ conductivity	0.1672 W m ⁻¹ K ⁻¹
Metal conductivity	3.18 W m ⁻¹ K ⁻¹
Reaction enthalpy	30900 J mol ⁻¹
Porosity	0.5
H ₂ density	0.0838 kg·m ⁻³
Initial metal density	4200 kg·m ⁻³
MH Saturated density	4264 kg·m ⁻³
Activation energy	21179.6 J·mol ⁻¹
Gas constant	8.314 J mol ⁻¹ K ⁻¹

2.4 Model validation

When cooling media temperature is 313 K, the average temperature variation at Z=15 mm and R=35 mm intercept point in the calculation domain is taken, and the model of this paper is compared with the experimental data of Jemni^[16] et al. The results are shown in Fig.2, and the current value is basically consistent with the literature value, and the maximum deviation does not exceed 1.25%, which verifies the reliability of the model.

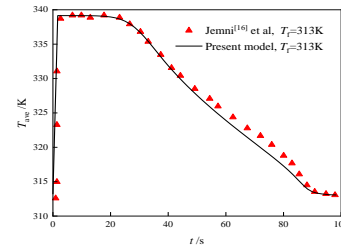


Fig.2 Model validation

3. RESULTS AND DISCUSSION

3.1 The effect of pressure on hydrogen absorption reaction

In order to investigate the effect of pressure on the characteristics of hydrogen absorption reaction. This paper uses the working conditions of inlet pressure p_{in} =0.6MPa, 1.2MPa, 1.8MPa and 2.4MPa for calculation respectively. The characteristic time of hydrogen absorption reaction is defined as the time t_{eq} when the hydrogen absorption amount reaches saturation. The variation of hydrogen absorption amount with time at different pressures is shown in Fig. 3. From Fig. 3, the

characteristic time t_{eq} at four pressures are 83.3 min, 50.8 min, 39.9 min and 34.0 min, respectively. It is obvious that the higher the inlet pressure the faster the reaction proceeds. The average temperature variation of the RB is shown in Fig. 4. It can be obtained that the average maximum temperature of the bed is also higher at higher pressures, which are 58°C, 78°C, 89°C and 98°C. High pressure corresponds to high reaction rate. Under the same heat exchange conditions, the reactor has a large heat production rate under high pressure conditions, and the RB temperature is the highest. Due to the fast reaction rate, the RB temperature under high pressure can also be reduced quickly. On the contrary, under low pressure, the initial heat production rate of the RB is smaller. The peak of the average bed temperature is also lower, but the reaction process is longer, the bed temperature decreases very slowly.

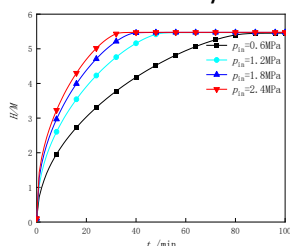


Fig. 3 Evolution of absorption reaction with external cooling ($h=1652 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$)

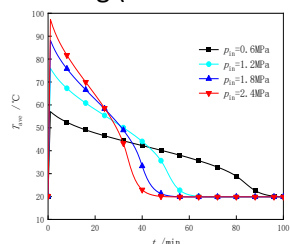


Fig. 4 Evolution of RB temperature with varying pressure and external cooling ($h=1652 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$)

Fig. 5 shows the distribution of the average RB temperature at $t_{eq}/2$. From the Fig.5, The temperature is higher far away from the convection cooling boundary, and the hydrogen absorption at these locations is also low accordingly. As the inlet pressure increases, the average bed temperature gradually increases. There is also a local high temperature concentration in the area far from the heat transfer boundary.

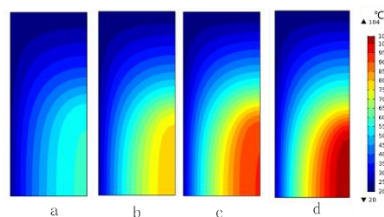


Fig. 5 Temperature distribution of RB with various pressures (a: $p_{in}=0.6\text{MPa}$, b: $p_{in}=1.2\text{MPa}$, c: $p_{in}=1.8\text{MPa}$, d: $p_{in}=2.4\text{MPa}$)

From the above discussion, we can get that the inlet pressure has a certain influence on both the hydrogen absorption rate and the bed temperature. From Fig. 4, we can get that in the initial stage of the reaction, the bed temperature rises rapidly to the maximum value. The higher the temperature, the higher the maximum value. Subsequently, under the same heat transfer boundary conditions, the higher the pressure, the faster the temperature decreases. For example, the temperature has dropped to the initial temperature in about 43 min at a pressure of 2.4 MPa while it takes nearly 100 min to gradually smooth out when the pressure is 0.6MPa. Therefore, a proper matching of low- and high-pressure operating conditions is considered to reduce temperature concentration. More effective thermal management of the reactor and further improvement of the reactor's hydrogen storage performance and safety.

3.2 Effect of pressure regulation on hydrogen absorption reaction

From the discussion of the results in the previous section. It is clear that the reactor has a fast reaction process under high pressure conditions, the initial local average temperature is high. When operating under low pressure conditions, the initial local average temperature is low, the reaction process is slow. For this reason, this section is further explored from the pressure-regulated operation to try to get the operation mode of low local average temperature combined with faster reaction process. Combining with Fig.4, taking $p_1=0.6\text{MPa}$ and $p_2=2.4\text{MPa}$, the average temperature intersection moment of the two pressure conditions operation, $t_0=32\text{min}$. at $t < t_0$, $p_{in}=p_1$, at $t > t_0$, $p_{in}=p_2$.

Fig. 6 shows the variation of hydrogen

absorption with time for the variable pressure operation condition. The characteristic time for the variable pressure run was 53.8 min, between 83.3 min (0.6 MPa) and 34 min (2.4 MPa). The overall reaction process was enhanced by about 65% compared to a single low pressure run. The average temperature variation of the RB with time for the corresponding conditions is shown in Fig. 7. During the short period of sudden pressure change to 2.4 MPa. The average RB temperature increased sharply and reached the highest value of 75°C, which was 23% lower than that at the inlet pressure of 2.4 MPa. In comparison, the variable pressure operation reduces the problem of low reaction rate and high local average temperature at single pressure operation mode.

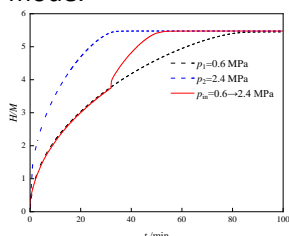


Fig. 6 Evolution of H₂ absorption reaction

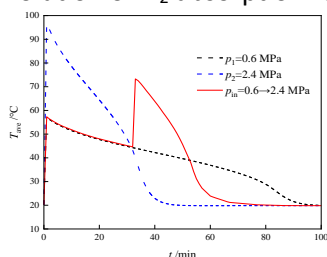


Fig. 7 Evolution of RB temperature

The inlet pressure was further adjusted based on the previous calculation where the inlet pressure was directly stepped from 0.6 MPa to 2.4 MPa. The three inlet pressure boundaries of a, b and c are shown in Fig. 8 were established. And the variation of their hydrogen absorption with time is compared and analyzed. From Fig. 9, it can be obtained that the characteristic times of the three pressure boundary conditions are between the highest pressure and the lowest pressure. t_{eq} are 54.7 min, 48.4 min and 46.1 min, respectively. Fig. 10 shows the variation of the average temperature of the bed with time under the three pressure boundaries. From Fig. 10, it can be obtained that the maximum temperatures corresponding to

the three boundaries of cases a to c are basically the same, all about 70°C. However, the temperature drop rate of case b and case c is greater than that of case a. The maximum values of the bed temperature under the three operating conditions of cases a-c are smaller than the average temperature at high pressure 2.4 MPa. This shows that proper dynamic adjustment of the inlet pressure has a facilitating effect on the hydrogen storage performance of the reactor. It can also avoid the local heat concentration inside the reactor, which is important to improve the reliability and safety of the reactor. From the distribution contour in Fig. 11, it can be seen that the region of larger hydrogen absorption under the three pressure boundary conditions is between high and low pressure. When the pressure boundary is case a, the hydrogen absorption performance is the best, the difference between case b and case c is not obvious, and the hydrogen absorption of case c is the worst.

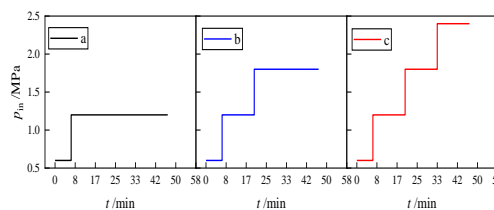


Fig. 8 Varying pressure arrangement (a: $p_{in} = 0.6 \rightarrow 1.2$ MPa, b: $p_{in} = 0.6 \rightarrow 1.8$ MPa, c: $p_{in} = 0.6 \rightarrow 2.4$ MPa)

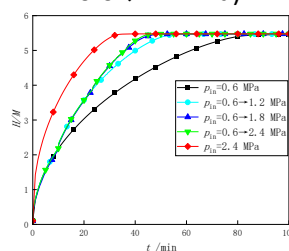


Fig. 9 Evolution of H₂ absorption reaction

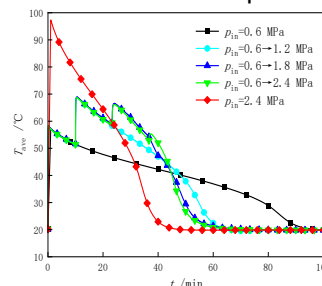


Fig. 10 Evolution of RB temperature

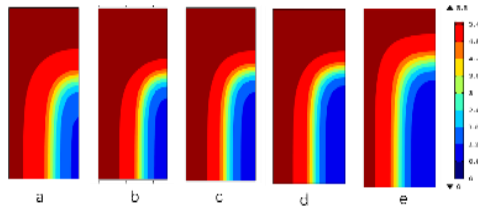


Fig. 11 Distribution of hydrogen absorption with various pressure (a: $p_{in}=0.6\text{MPa}$, b: $p_{in}=2.4\text{MPa}$, c: $p_{in}=0.6\rightarrow 1.2\text{MPa}$, d: $p_{in}=0.6\rightarrow 1.8\text{MPa}$, e: $p_{in}=0.6\rightarrow 2.4\text{MPa}$)

4. CONCLUSION

In this paper, a multi-field coupled model of heat-mass transfer and reaction kinetics is developed for the MH reactor. The hydrogen absorption characteristics are carried out from the perspective of pressure regulation. The main research results and conclusions are summarized as follows.

(1) The coupled model for the heat-mass transfer and thermochemical process has been validated. The external cooling method can remove the reaction heat quickly and ensure a fast absorption evolution and a mild temperature in RB. When the pressure increased from 0.6 MPa to 2.4 MPa, the reaction time reduced from 83.3 min to 34 min

(2) Compared with a constant pressure operation, the various pressure mode contributes to reducing the peak temperature of RB from 98°C to 75°C. A suitable pressure regulation mode was established and the local overheating problem of the metal hydride RB is effectively mitigated.

(3) The coupled effect of reaction and heat transfer is considerable and some regulations are necessary. This paper provides a guidance with pressure regulating operation for MHHS technology.

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