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Multi-level configuration and optimization of a thermal energy storage system using a metal hydride pair^{\star}

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HIGHLIGHTS

- A thermal energy storage system using a metal hydride pair is designed.
- The simplified model enables more efficient and time-saving computations.
- The intensification mechanism of multi-level configuration is clarified.
- Optimum number of levels is determined according to the effect of number of levels.
- Optimum allocation principle of storage materials in multi-level system is revealed.

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Metal hydride thermal energy storage (TES) system is an attractive option for the concentrated solar power. In this article, a multi-level configuration is proposed to intensify the discharging process of TES system using $MgH_2/LaNi_5$ pair. The discharging process is simulated by establishing a mathematical model, which is solved by COMSOL Multiphysics v5.1. The multi-layer structure of storage units is simplified by the conversion of porosity and thermal conductivity. It is found that the multi-level configuration mitigates the non-uniform reaction along the oil flow direction so as to enhance the overall discharging performance effectively, such as the decrease of discharging time from 17,350 s to 14,688 s and the increase of output temperature by ~5 °C. Meanwhile, the optimum number of levels is determined between 4 and 5 according to the effect of the number of levels on the discharging performance. Furthermore, it is revealed that the optimum allocation principle of storage materials is to maintain the same discharging time for all the subsystems.

1. Introduction

With the gradual flourish of concentrated solar power (CSP) market in recent years, there is an urgent need to develop efficient materials for high temperature thermal energy storage (TES), which enables the CSP plants to produce continuous and dispatchable electricity [1]. Energy storage density is an important indicator to evaluate the TES materials [2]. Although the sensible heat materials have been successfully utilized in some CSP plants [3], their energy storage densities are quite low such as Solar Salt (110 kJ kg^{-1}) and Hitec (156 kJ kg^{-1}) [4]. At present, attentions are paid to the phase change materials with the high latent heat such as NaNO₃ (199 kJ kg^{-1}) and MgCl₂ (452 kJ kg^{-1}) [5], but the low thermal conductivities and high temperature corrosion restrict the application in the industrial-scale CSP plants [6,7]. Additionally, the thermochemical heat storage has also been taken into consideration due to their outstanding reaction enthalpy such as MgH_2 (2814 kJ kg⁻¹), Ca(OH)₂ (1411 kJ kg⁻¹) and Co₃O₄ (844 kJ kg⁻¹) [8–10].

In particular, Mg-based metal hydrides are considered as a promising option for high temperature TES materials because of their low cost, good reversibility and cyclic stability [11]. The properties of Mgbased metal hydrides for the high temperature TES are listed in Table 1. Since the pure MgH₂ has low thermal conductivity and slow kinetics [12], many kinetic improvements have been reported, in which the ball-milling with elements has been broadly recognized and used [13]. Bogdanović et al. [12] found that Ni-doped MgH₂ has faster kinetics, lower equilibrium pressure and higher energy density (2.257 MJ kg⁻¹) as compared to the pure MgH₂. It is worth mentioning that the

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Nomenclature		и	flow velocity of water/oil, $m s^{-1}$	
		Ws	total weight of material, kg	
Abbreviation		wt	saturated mass content of H in the metal hydride	
		Χ	reaction fraction	
CSP	concentrated solar power			
HTF	heat transfer fluid	Greek letters		
TES	thermal energy storage			
GEOR	gravimetric exergy-output rate	ε	porosity, K^{-1}	
HTP	heat transfer pipe	λ	thermal conductivity, Wm^{-1}	
		β	growth rate of GEOR	
Symbols		ρ	density, kg m ^{-3}	
		μ	dynamic viscosity, Pa s	
Α	area, m ²	δ	drop degree of water temperature	
$C_{\rm a}$	H_2 absorption/desorption rate constant, s ⁻¹			
c_{pg}	specific heat of hydrogen gas, $J kg^{-1} K^{-1}$	Subscripts		
C _{ps}	specific heat of metal hydride, $J kg^{-1} K^{-1}$			
c_{pf}	specific heat of heat transfer fluid, $J kg^{-1} K^{-1}$	0	initial value	
C _s	saturated molarity of H_2 in the metal hydride, mol m ⁻³	d	discharging process	
$D_{\rm o}/D_{\rm i}$	outer/internal diameter, m	ea	equilibrium for H ₂ absorption	
$E_{\rm a}$	activation energy of H_2 absorption/desorption, kJ mol ⁻¹	f	heat transfer fluid	
$E_{\mathbf{x}}$	exergy, W	i	inner diameter	
H	height, m	out	outlet of HTP	
ΔH	enthalpy of reaction, $J \mod^{-1}$	S	saturation	
L	length of heat/hydrogen storage unit, m	axial	axial direction of compacts	
Μ	compact number per heat/hydrogen storage unit	с	compact	
р	pressure, Pa	e	equivalent value	
R	universal gas constant, J mol ⁻¹ K ⁻¹	ed	equilibrium for H ₂ desorption	
t	time, s	g	hydrogen gas	
$\Delta t_{\rm d}$	discharging time difference, s	0	outer diameter	
Т	temperature, K or °C	ref	reference value	
S	molar reaction rate, $mol m^{-3} s^{-1}$	W	HTP wall	
ΔS	reaction entropy, $J \mod^{-1} K^{-1}$	radial	radial direction of compacts	

operating temperature of MgH₂ cannot exceed ~450 °C due to its high temperature sintering phenomenon [8]. Mg₂FeH₆ has relatively higher operating temperature and lower equilibrium pressure. However, due to its difficult synthesis condition, the reactive mechanical alloying needs to be used and the corresponding yield is only 15.6% at room temperature [14]. Li et al. [15] recently synthesized Ce₂Mg₁₇ by rapid solidification and found it has much lower equilibrium pressure than that of Mg₂FeH₆ at the high temperature of 400 °C. Sheppard et al. [16] found that NaMgH₃ has the storage advantages of high enthalpy, flat plateau and negligible hysteresis but its reversibility is hindered due to the two-step dehydrogenation. Thus, the doped MgH₂ are currently the most widely used material for the demonstrations of TES system due to their comprehensive performance.

In addition to material development, the study on TES system is also importantly related to the real volumetric energy density, charging/ discharging performance and so on. Hydrogen storage device is necessary for the metal hydride TES system since there are hydrogen desorption and absorption during the charging and discharging cycles. According to different hydrogen storage methods, the metal hydride

Table 1 Properties of Mg-based metal hydrides for the high temperature TES.

Metal hydrides	Operating temperature/°C	Equilibrium pressure/MPa	Practical energy density/MJ kg ⁻¹	References
$\begin{array}{l} MgH_2 + 2\% Ni\\ Ce_2 Mg_{17}\\ Mg_2 FeH_6\\ NaMgH_3 \end{array}$	290–420	0.1–2.5	2.257	[8]
	350–450	0.3–2.34	1.402	[15]
	450–550	2.8–13.8	1.817	[8]
	475–575	0.1–1.0	1.429	[16]

TES systems have two types, namely integration with a pressure vessel and with a low temperature metal hydride reactor, respectively. Paskevicius et al. [17] conducted an experimental study on the charging and discharging cycles of a MgH₂ TES prototype, which is stable enough to be applied to the practical operation of a CSP plant. Bao et al. [18] investigated the discharging performance of TES system with a pressure vessel by numerical simulation. A multi-step operation mode was used to reduce the output temperature fluctuation. The real volumetric energy density of TES system with pressure vessel has no obvious benefits as compared to that of two-tank molten salt storage under the acceptable energy consumption of hydrogen compression. In contrast, the TES system using a metal hydride pair is most likely to achieve industrial applications. Bogdanović et al. [19] designed the first pilotscale MgH₂ TES system using the alloy 5800 as hydrogen storage material, which generated superheated steam up to 330 °C during the discharging process. Meng et al. [20] conducted a theoretical study on the application of MgH2 TES system in a CSP plant, which indicated that the discharging process of TES system was mainly controlled by the heat transfer performance. During the discharging process, the temperature difference between heat transfer fluid (HTF) and reaction bed decreases along the HTF flow direction due to the inherent HTF temperature rise. The corresponding heat transfer degrades along the HTF flow direction, especially the heat transfer deteriorates at the HTF outlet. This leads to the decrease of reaction rate along the HTF flow direction so that the overall discharging performance degrades such as the decrease of output temperature and the increase of discharging time. Therefore, a multi-level configuration is proposed by authors to intensify the discharging process of metal hydride TES system. Furthermore, the optimum number of levels and optimum allocation principle in the multi-level system need to be determined.

In this article, the discharging process of a TES system using $MgH_2/$

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