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To cite this article: Lingkang Jin *et al* 2023 *J. Phys.: Conf. Ser.* **2648** 012056

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Metal hydrides in hydrogen storage: optimization of dynamic control strategies

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Abstract. Metal hydrides have emerged as a promising solution for efficient hydrogen storage in solid matter. While the charging and discharging kinetics of these systems are well-known, dynamic control strategies from a system's perspective still need a detailed analysis by the scientific community. In this research work, a metal hydrides system and its dynamic controls have been numerically studied. AB₂-type metals (ZrMn₂) are involved as a storage medium, which is coupled to a conditioning system via a heat pump and a hydrogen compressor; therefore, both operating temperature and pressure can be controlled. Results showed that hydrogen pressure is a fundamental component in accelerating reaction dynamics and increasing stored mass. However, it is also the most energy-intensive component. The use of a conditioning system, which works at a proper set temperature, can reduce the hydrogen compressor energy to achieve the same performance, although requiring higher power input from the heat pump's compressor. Furthermore, the operational strategy must be chosen based on either the minimization of charging/discharging time or energy expenses.

Nomenclature

Subscripts

<i>a</i>	Absorption
<i>d</i>	Desorption
<i>eq</i>	Equilibrium phase
<i>f</i>	Conditioning fluid
<i>H₂</i>	Hydrogen
<i>in</i>	Inlet
<i>lim</i>	Limitation
<i>out</i>	Outlet
<i>s</i>	Solid/Metal alloy

Variables

\dot{m}	Mass flow rate [kg/s]
ϵ	Heat transfer efficiency [-]

<i>c</i>	Specific heat capacity [J/kg K]
<i>E</i>	Activation energy [kJ/mol]
<i>H</i>	Enthalpy [J/mol]
<i>h</i>	Specific enthalpy [J/kg]
<i>K</i>	Kinetic constant [s ⁻¹]
<i>m</i>	Mass [kg]
<i>MW</i>	Molecular weight [kg/mol]
<i>P</i>	Gas pressure [bar]
<i>R</i>	Gas constant [J/mol K]
<i>S</i>	Entropy [J/mol K]
<i>T</i>	Temperature [K]
<i>t</i>	Time [s]
<i>X</i>	Weight concentration (%)



1. Introduction

One of the major bottlenecks in using hydrogen as an energy carrier is its storage due to its low density (0.082 kg/m^3 at standard conditions), which is almost 9/10 times lower than the natural gas one [1]. Viable solutions for hydrogen storage at extremely high pressures ($> 200 \text{ bar}$) could be either in its liquefied form, or by its conversion into another composite [2]. Additionally, hydrogen can be also stored in solid form using specific metal alloys that capture and release hydrogen, thus forming the so-called metal hydrides [3]. Different materials can be applied with different temperatures and weight concentration ranges [4]. Several researchers in material science have investigated kinetic improvements. Luo et al. [5] performed a kinetics assessment of the magnesium-based metal alloy, while Santecchia et al. [6] did a similar work on a metal-polymer composite, both of them focusing on the hydrogen storage purpose.

While there is a rather extensive research on the hydrogenation-dehydrogenating process, to the authors' knowledge there is a lack of systematic analyses of these technologies integrated with other energy systems. Therefore, this work presents an overview of metal hydrides system control strategies and their effects coupled with an hydrogen source, as well as an hydrogen compressor and a conditioning system to adjust pressure and temperature properly. By examining these aspects, this study aims at contributing to a more comprehensive understanding of the potential of metal hydrides systems for hydrogen storage in energy applications.

2. Materials and methods

Metal hydrides refer to a class of metals that capture and release hydrogen, forming a compound with the metal through a chemical reaction. The driving force for charging and discharging is the pressure difference between the gaseous hydrogen and the metal's equilibrium pressure. The latter is defined by the P-X-T diagram (see Figure 1), which provides information about the equilibrium pressure based on: i) whether it is charging or discharging, ii) system temperature, and iii) hydrogen weight concentration. This information is extracted from experiments on the material characterization.

The hydrogen storage system typically consists of a pressurized tank containing metal powders. Based on the pressure of the gaseous hydrogen at the inlet/outlet sections, the system is either charging or discharging (see Figure 2).

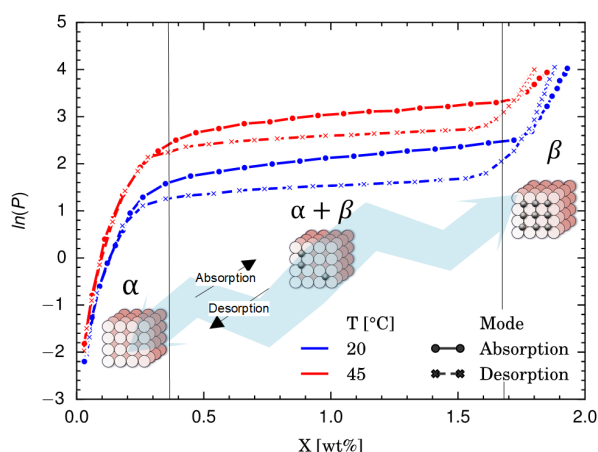


Figure 1. Metal hydrides exist: i) solid solution phase, ii) metal-hydrogen solution phase, and iii) hydrides phase (all of them driven by pressure)

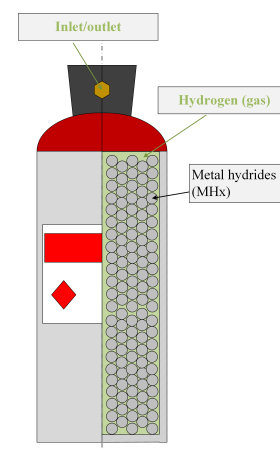


Figure 2. Metal hydrides hydrogen storage system: pressurized hydrogen is injected into the tank where the metal powder is contained

2.1. System's layout and operation stages

The system's layout for both charging and discharging stages is shown in Figure 3 and it can be divided into three zones:

- (i) hydrogen pressure control zone: in the charging phase, the pressure is managed by the hydrogen compressor, while the pressure in the discharging phase is set based on the hydrogen consumption request (fuel cell);
- (ii) metal hydrides system: it presents an exothermic behaviour in the charging phase and endothermic one in the discharging phase;
- (iii) temperature control zone: this area involves the conditioning system of the metal hydrides system, which has to cool the metal hydrides down during the charging and warm them up during the discharging stage. The application of the heat pump is used to supply both heating and cooling energy when required;

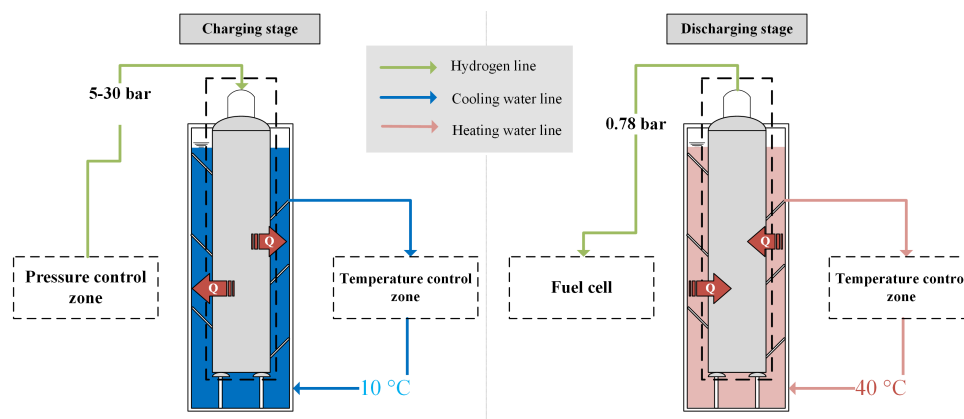


Figure 3. System's layout for both charging and discharging phases

The operational parameter ranges are listed in Table 1 where the conditioning water temperature is 10C in the absorption phase and 40C in the desorption one. The system's temperature is fixed and chosen from a predefined set.

Table 1. Operation parameters' range

	Absorption	Desorption
X [%]	0.2→ 1.5	1.6→ 0.2
Pressure [bar]	15, 20, 25	0.78
Setting temperature [°C]	15, 20, 25	20, 25, 30, 35
Water temperature [°C]	10	40
Heat pump refrigerant type		R134a
Heat pump refrigerant temperature [°C]	5-15	50-70
Overall heat exchangers efficiency [-]		0.8
Hydrogen compressor efficiency [-]	0.8	n.a.

2.2. Metal hydrides numerical modeling

The numerical modeling of the metal hydrides hydrogen storage consists of two steps:

- (i) The parametrization of the experimental data, provided by the metal hydrides system's manufacturer, involves the assessment of the metal's technical properties through a polynomial fitting method. This method determines the equilibrium pressure function with changing concentration (X) and temperature, providing information on its value at operating conditions not directly obtained in the experiments. Similar approaches were used by Hariyadi et al. [7] and Talagañis et al. [8].

To enable the dynamic evaluation, specific technical parameters of the material such as enthalpy variation must be known a priori. Hence, a parametrization process using the P-X-T diagram and the Vant'hoff plot (described in Dornheim's work [9]), which is also reported in Hariyadi's work [7], is used with the relationship stated in Eq. 1.

As for the kinetic parameters of the metal, they cannot be derived from the P-X-T curve due to the absence of the time variable. Therefore, in this study the kinetic parameters are sourced from the scientific literature [8].

$$\ln(P) = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (1)$$

- (ii) The numerical modeling of the kinetics of the metal hydrides system relies on ordinary differential equations to establish mass and energy balances. The equations used in this work are based on the by various researchers (Gambini et al. [10, 11] and Talagañis et al. [8]).

The mass concentration variation within the solid is described by the following equation with its upper limit occurring during the charging phase, specifically when the β phase has been reached, while for the discharging stage such limit is equal to zero.

$$\frac{dX}{dt} = K_{a,d} e^{-\frac{E_{a,d}}{RT}} \cdot \ln\left(\frac{P}{P_{eq}}\right) \cdot |X_{lim} - X| \quad (2)$$

This can be converted into solid hydrogen mass using the definition of X , which is defined as the mass ratio:

$$X = \frac{m_{H_2}}{m_{H_2} + m_s} \quad (3)$$

therefore, the mass balance of the gaseous hydrogen is expressed as follows:

$$\frac{dm_{H_2,g}}{dt} = -\frac{d(X \cdot (m_{H_2} + m_s))}{dt} + \dot{m}_{H_2,in} - \dot{m}_{H_2,out} \quad (4)$$

Under the assumption of an ideal scenario, where the mass of the gaseous form of hydrogen within the metal hydrides system remains constant, the hydrogen mass flow balance is defined as follows:

$$\dot{m}_{H_2,in} - \dot{m}_{H_2,out} = \frac{d(X \cdot (m_{H_2} + m_s))}{dt} \quad (5)$$

Finally, the energy balance can be expressed by Eq. 6, where the specific heat capacity of the system includes both solid and gaseous hydrogen (see Eq. 9).

$$C \frac{dT}{dt} = -\frac{\Delta H}{MW_{H_2}} \frac{d(X \cdot (m_{H_2} + m_s))}{dt} + \dot{m}_f c_f \epsilon (T_f - T) + \dot{m}_{H_2,in} \cdot h_{in} - \dot{m}_{H_2,out} \cdot h_{out} \quad (6)$$

$$C = (m_{H_2g} \cdot cp_{H_2} + (m_{H_2} + m_s) \cdot cp_s) \quad (7)$$

However, for the scope of this work, it is assumed to have a constant supply pressure; as a consequence, the temperature of the system must remain constant over time:

$$\dot{m}_f c_f \epsilon (T_f - T) = \frac{\Delta H}{MW_{H_2}} \frac{d(X \cdot (m_{H_2} + m_s))}{dt} - \dot{m}_{H_2, in} \cdot h_{in} + \dot{m}_{H_2, out} \cdot h_{out} \quad (8)$$

Additionally, since the solid mass of the hydrogen (m_{H_2}) can reach up to 1.6 – 2% of the metal mass (for AB₂-type metals), its contribution to the overall mass can be neglected.

$$(m_{H_2} + m_s) \approx m_s \quad (9)$$

2.3. Performance indicators

The following indicators have been used to evaluate the performance of different operational conditions from both economic and control perspectives:

- The time required to reach the pre-defined weight concentration condition, indicating the amount of hydrogen stored or discharged (Table 1), is considered as one performance indicator.
- Another sets of indicators are the energy consumption of the heat pump and the hydrogen compressor during the capture and release of hydrogen. These indicators are linked together and provide preliminary insights into the operating cost of the entire process.

3. Results and comments

The results of the dynamics in both phases are presented and discussed in Figures 4 and 5. In the charging phase, the hydrogen gas is injected at the inlet with the set pressure. The exothermic nature of the absorption process, along with the gaseous hydrogen inlet, leads to an increase in the system temperature, but the conditioning system compensates it by controlling the water mass flow rate (heat transfer fluid) flowing through the storage system. Conversely, in the discharging phase, the dynamics are similar but reversed with the conditioning system working to recover the temperature drop. Moreover, the concentration variations differ between the absorption and desorption stages that are influenced by the kinetic and activation energy parameters. As a consequence, the required thermal energy varies significantly between the two phases with the desorption one requiring a lower thermal energy.

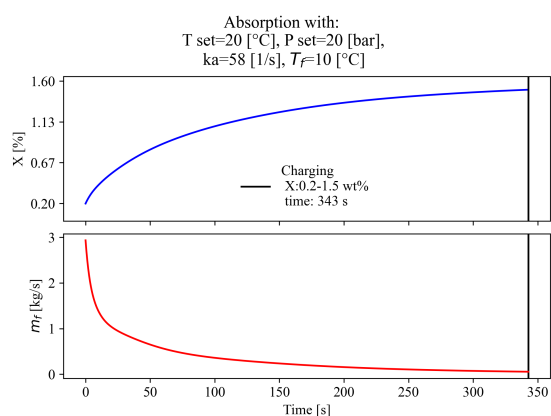


Figure 4. Absorption phase dynamics

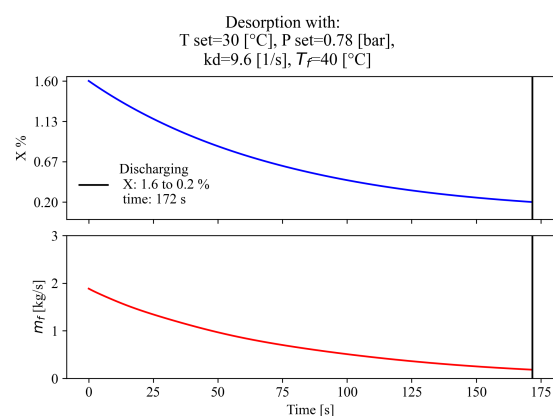


Figure 5. Desorption phase dynamics

Numerous combinations of the operational parameter sets are explored to provide a comprehensive understanding of the performance indicators as shown in Figures 6 and 7. When

only one controllable parameter is considered, the influence of changing operational conditions is straightforward. Indeed, for the desorption phase, the dynamic indicator and the energy indicator form a Pareto-curve shape where both indicators cannot be minimized at the same time. However, the absorption phase presents a more complex situation due to the presence of multiple controllable parameters, including temperature and pressure. Additionally, their associated energy consumption is connected with the dynamics. It is observed that, to store the same amount of mass, the dominant parameter for the dynamics is the pressure; indeed, over a certain pressure threshold (e.g., 15 bar), the set temperature would not affect the charging time considerably. Moreover, under such a pressure threshold, the system cannot reach the targeted charged mass due to the low-pressure gap. By reducing the system set temperature, not only the energy dedicated to the heat pump compressor is reduced, but also the hydrogen compressor would benefit from it since the charging time lowers.

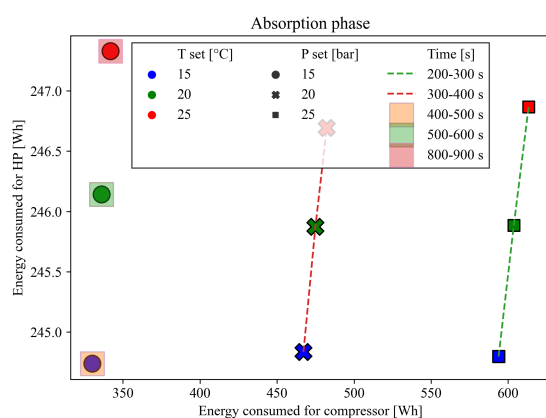


Figure 6. Performance indicators in the absorption phase. Data are categorized into three levels, with various colors representing different set temperatures (blue, green, and red), distinct shapes indicating setting pressures (circle, cross, and square), and dotted lines denoting the time needed for charging. Additionally, for data that are not aligned with the same time interval as others, a transparent squared frame is employed to signify the time frame

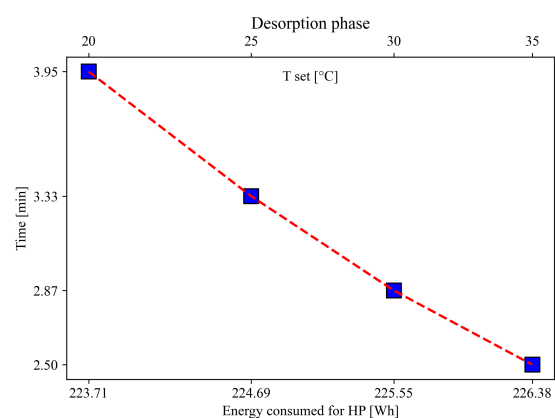


Figure 7. Performance indicators during desorption. Compared to the absorption phase, the results are straightforward as they are showing a Pareto curve shape indicating that it is not possible to optimize both dynamics and energy consumption simultaneously

4. Conclusions

This study focused on exploring dynamic control strategies for a metal hydrides (AB_2 type) system used for hydrogen storage. The numerical modeling was based on experimental results characterizing the P-X-T diagram provided by the system supplier. During the absorption phase, it was observed that hydrogen pressure played a significant role in shortening the processing time compared to the impact of conditioning temperature, even though it leads to a higher energy consumption by the hydrogen compressor. To mitigate the hydrogen compressor's energy expense, a possible approach would be the use of a lower system set temperature, despite the consequence of an increase in the heat pump power. However, the consumed energy is anyway reduced due to time reduction of the process. In the desorption phase, the achievement of a faster hydrogen release would entail in higher expenses to cover the cooling energy supply. Finding an

optimal operational strategy for both phases is not straightforward, and further investigation of system controllers, including experimental testing to determine material kinetic parameters and activation energy, will be addressed in future researches.

Appendix

All modeling parameters are reported, in Table 2.

Table 2. Modelling parameters

	Values	Description	ref.
R	8.31	Universal gas constant [J/mol K]	-
T	15-35	System initial temp [°C]	-
$P_{charging}$	5-30	System charging pressure [bar]	-
$P_{discharging}$	0.78	System discharging pressure [bar]	-
k_a	58	Absorption kinetics [s^{-1}]	[8]
k_d	9.6	Desorption kinetics [s^{-1}]	[8]
x_d	1.6	Initial state of discharging [%]	P-X-T curve
x_a	0.2	Initial state of charging [%]	P-X-T curve
m_s	15500	Metal alloy mass [g]	Datasheet
cp_s	355	Specific heat of metal [J/kg K]	[8]
cp_{H_2}	14300	Specific heat of gaseous hydrogen [J/kg K]	-
MW_{H_2}	0.002	Molecular weight of hydrogen [kg/mol]	-
c_f	4181.3	Specific heat of the conditioning water [J/kg K]	-
T_f	10 or 40	Fluid temperature [°C]	-
E_a	21.17	Absorption activation energy [kJ/mol]	[8]
E_d	16.42	Desorption activation energy [kJ/mol]	[8]
ϵ	0.8	Heat transfer efficiency [-]	-

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