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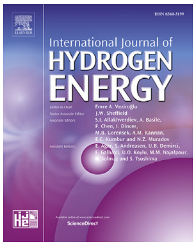

Automation and analysis of the operation of $(La_{0.85}Ce_{0.15})Ni_5$ in energy storage plants

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ABSTRACT

The hydrogen storage phase of an energy storage plant based on metallic hydrides has a strong influence on the total efficiency of storage power plants as well as on their response time. The technique presented in this paper uses a hydrogen-metal chemical bond during its storage. This paper describes a metal hydride cylinder modeled and simulated by using the main quantities involved in the adsorption and desorption processes as well as in an analysis of the influence of thermal quantities involved in these processes. As a result, a proposal for automation of the thermal exchange of the modeled cylinder is presented and the possibilities of evaluation of this technique.

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Introduction

The generation of electricity from renewable sources is intermittent due to the characteristics of primary energy (sun, wind, water, etc.) and can cause oscillations and distortions in the voltage levels compromising quality, stability and reliability of the energy produced whenever it has to be connected to the electrical system. In the case of energy storage acting as a standalone or connected generating source to the public network, there may be an increased penetration of these sources in the energy matrix. For large scale applications of these clean energies, one of the greatest challenges is the large scale energy storage, which requires new, low-cost and eco-friendly conversion and storage systems. These requirements demand development of intensive researches in hydrogen storage [1]. An advantage of hydrogen for energy storage is that the stock can be stored for months or years and its self-discharge is very slow as well as its environmental impact. The power density is one of the highest among other power storage means, around 500 W/kg with energy density ranging from 100 to 10000 Wh/kg. The life of the hydrogen-based energy storage plants is between 15 and 20 years and supports 20,000 charge cycles with a short operating time in the order of seconds.

Hydrogen storage can happen in three states, i.e., high-pressure gas, cryogenic liquid hydrogen, and solid-state materials [2]. These hydrogen storage technologies differ primarily in terms of efficiency, energy density, leakage proofing, levels of development, safety and installation complexity, Table 1.

One of the most promising hydrogen storage technique is the compression of gas in high-pressure cylinders. In this condition, the mass of the stored hydrogen lies in between 6 and 10% of the total mass of the cylinder at pressures of 35–70 MPa. Although commercially available, this form of storage has a high cost, is very energy demanding, and its

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Nomenclature

(')	Indicates that the variable is written in relation to the volume of MH $\left(\frac{1}{v_{HM}}\right)$
A_{w-MH}	water-MH heat transfer area (m^2)
C_a	constant for hydrogen adsorption rate (1/s)
C_d	constant for hydrogen desorption rate (1/s)
$C_{p,H}$	specific heat of hydrogen (J/kg K)
$C_{p,s}$	specific heat of solid (J/kg K)
$C_{p,w}$	specific heat of water (J/kg K)
E_a	activation energy for hydrogen adsorption (J/mol)
E_d	activation energy for hydrogen desorption (J/mol)
E_{w-MH}	thermal energy exchanges water-MH (MJ)
$\dot{H}_{Max}$	maximum volume of hydrogen stored by the alloy (L/kg)
$\frac{H}{H_{max}}$	rate of occupation (rate between the amount of stored hydrogen and the maximum storage capacity)
$\dot{m}_{H,cyl}$	hydrogen cylinder mass flow rate (kg/s)
$\dot{m}_{H,MH}$	hydrogen mass flow (adsorbed or desorbed) (kg/s)
$\dot{m}_{w,cyl}$	mass of water circulating in the cylinder per unit time (kg/s)
P_0	reference pressure (Pa)
$P_{H,MH}$	hydrogen pressure (Pa)
$P_{H,MH,i}$	initial hydrogen pressure (Pa)
P_{eq}	equilibrium pressure (Pa)
Q_{w-MH}	thermal power exchanges water-MH (W)
R_H	specific hydrogen constant (J/kg K)
R_u	universal gas constant (J/mol K)
$T_{MH,i}$	initial temperature of the metal hydride (K)
T_{MH}	metal hydride temperature (K)
$T_{w,in}$	water temperature at the cylinder inlet (K)
$T_{w,out}$	water temperature at the cylinder outlet (K)
$T_{w,stor,i}$	initial water temperature stored (K)
$T_{w,stor}$	stored water temperature (K)
V_{pump}	pump speed (%)
$\dot{v}_{H,MH}$	hydrogen MH volumetric flow rate (L/min)
$\dot{v}_{H,cyl}$	hydrogen cylinder volumetric flow rate (L/min)
v_{MH}	volume of the alloy (m^3)
v_t	volume metal hydride tank (m^3)
$\rho_{g,i}$	initial density of gas in metal hydride (kg/m^3)
ρ_g	density of gas in metal hydride (kg/m^3)
$\rho_{s,i}$	initial density of the solid (kg/m^3)
ρ_s	density of the solid (kg/m^3)
ρ_{s0}	density of an empty metal hydride (kg/m^3)
ρ_{ss}	density of the saturated solid (kg/m^3)
m_{MH}	mass of the alloy (kg)
U	overall heat transfer coefficient for the alloy (W/m^2K)
$a, b, \varnothing, \varnothing_0, \alpha_1, \alpha_2, \beta$	constant that represent the isothermal curves (PCT) of hydride metal
ε	porosity of the alloy
$\Delta H_{a,m}$	change enthalpy for hydrogen adsorption (J/kg)
$\Delta H_{d,m}$	enthalpy change for hydrogen desorption (J/kg)
$\Delta H_{d,mo}$	enthalpy change for desorption hydrogen (J/mol)
$\Delta S_{d,mo}$	entropy change in for desorption hydrogen (J/mol K)
ρ_H	density of hydrogen in NTP (kg/L)

losses reach 30%. It also has problems with safety (mechanical fracture) and needs compressors to fit them into hydrogen cylinders [3].

Hydrogen in liquid form has the highest density and storage in this state, results in a compact hydrogen storage means. In practical terms, hydrogen is stored in cryogenic tanks under pressures of 0.1 MPa and at temperatures of -253 °C. Under these conditions, the mass of the stored hydrogen corresponds to 20% of the mass of the cylinders. The disadvantages of this method are the problems related to the amount of energy required for hydrogen liquefaction and losses by evaporation reaching 40% of the energy contents [2,3].

The hydrogen storage technology in metal hydrides presents the advantages of simplicity in both design and operation, absence of moving parts, compactness, safety, long lasting, reliability and the possibility of consumption of the industrial waste heat instead of electrical energy. In short terms, this method consists of making a chemical bond between hydrogen and a metal (or metal alloy), thereby storing the hydrogen as metal hydride.

The store materials must have high hydrogen storage capacity, fast hydrogenation/dehydrogenation kinetics and low economical cost [4]. The chemical bond can be undone by changing the thermodynamic quantities (pressure and temperature) to the hydrogen contents be recovered. In this paper, a metal hydride cylinder is modeled and simulated using the main quantities involved in the adsorption and desorption processes as well as established an analysis of influence of the thermal quantities in these processes. Finally, it is proposed the automation of the thermal exchange between the modeled cylinder and the external means together with a reunion of the achieved results.

Metal hydride

The typical relationship of formation of metal hydride is shown in equation (1).

$$M(s) + {}^{x}\!/\!{}_{2}H_2(g) \underset{desorption}{\overset{adsorption}{\rightleftarrows}} MH_x(s) + Q \tag{1}$$

where M is a metal alloy ($LaNi_5$, TiFe, etc.) and the indices (s) and (g) refer to the solid and gas phases, respectively [5].

Table 1 – Characteristics of the different hydrogen storage states [6].

Form of storage	Metal hydride		Compressed gas		Liquid	Activated carbon (77 K)
	<100 °C	>300 °C	300 bar	700 bar		
Energy Density (MJ/kg)	0.9–0.933	0.79–0.83	0.915	0.905	28–45	8–10
Efficiency (%)	0.9–0.933	0.79–0.83	0.915	0.905	0.625–0.77	0.917–0.933
Leakage (%/day)	≈0	≈0	0.000024	0.000033	1	0.2

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