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Metal hydrides reactors with improved dynamic characteristics for a fast cycling hydrogen compressor

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Abstract. This paper presents an investigation of coupled heat and mass transfer process in metal hydrides hydrogen storage reactors. Hydrogen storage and compression performance of our designed and developed reactors are studied by varying the operating parameters and analyzing the effects of metal hydride bed parameters. The metal alloy selected to characterize the cycling behaviour of reactors is LaNi$_5$, material synthesized and characterized by us in the range 20-80°C. Four types of metal hydride reactors were tested with the aim to provide a fast hydrogen absorption-desorption cycle, able to be thermally cycled at rapid rates. Some new technical solutions have been studied to make a step forward in reducing the duration of the reactors cycle, which combines the effective increase of the thermal conductivity and good permeability to hydrogen gas. Dynamic characteristic of developed fast metal hydride reactors is improved using our novel mixture metal hydride-CA conductive additive due to the increased effective thermal conductivity of the alloy bed. The advanced hydride bed design with high heat transfer capabilities can be thermally cycled at a rapid rate, under 120 seconds, in order to process high hydrogen flow rates.

1. Introduction
The major challenges for hydrogen to become a successful energy vector in the future consist in developing of new and efficient technologies in hydrogen production, storage and in the end uses. Technologies considered under this goal include: improving hydrogen production technologies, developing innovative ideas for hydrogen transport and storage, able to be employed in very practically purpose like engine supplies and fuel cells [1,2].

It is known that hydrogen storage represent a technological challenge in developing hydrogen economy. Among the different hydrogen storage methods, reversible metal hydrides are considered as an efficient volume medium for hydrogen storage, offering safe, low pressure and high energy density. Whatever particular hydrogen storage method is selected, the efficient hydrogen compression is an unavoidable step. Hydrogen compressors based on the reversible absorption/desorption ability of metal hydrides are now intensively studied [3,4], and can reach high hydrogen delivery pressure with many advantages: high reliability and low maintenance, low energy costs and conserve the purity of the hydrogen. Usage of the metal hydrides to hydrogen thermal compression, employment the thermodynamic characteristics of hydrogen absorbent alloys: the equilibrium pressure $P_{eq}$ variation with temperature $T$ is descript by van’t Hoff equation:
where: $\Delta H$ and $\Delta S$ are the enthalpy and entropy variation and $R$ is the ideal gas constant.

The selection of alloys employed in hydrogen storage and compression depend on their properties. If for storage devices, the alloys with high absorption capacity and a good hydrogen absorption-desorption kinetics are appropriate, in the case of compression devices based on metal hydrides the most important properties are: the good hydrogen absorption-desorption rate, a smaller process enthalpy, great structural stability during the cycles. In this case are needed alloys with big differences between the hydrogen absorption and desorption pressures at equilibrium at small temperature differences. The hydrogen thermal compression using a metal hydride is essentially a two-step process. Figure 1 shows the principle of operation for a single stage compressor.

![Figure 1. Principle of operation of a single stage hydrogen metal hydride compressor.](image)

To realize an efficient hydrogen thermal compressor, the main goal of our researches, it is essential to develop fast cycling metal hydride reactors (FMHR). The most important characteristics of a hydrogen storage reactor suitable for a metal hydride based compressor are: a high thermal conductivity of the hydrogen storage bed and a good permeability for hydrogen gas. To aim a short duration of an absorption-desorption cycle, FMHR requires a rapid mass (hydrogen gas) and heat transfer. These can be previously hindered by the following constraints: (i) heat transfer through a metal hydride powdered bed is inherently poor; (ii) hydrogen pressure drops through the hydride beds may become so excessive that gas transfer is seriously impeded.

2. Experimental
The metal alloy selected to characterize the cycling behavior of FMHR is LaNi$_5$, synthesized by IMNR Bucharest and characterized by us, in the range 20-80°C. The pressure composition isotherm (p-c-T) for LaNi$_5$, measured by a house-built volumetric Sievert installation, is shown in figure 2. We designed and built four types of metal hydride reactors which were tested with the aim to provide a fast hydrogen absorption-desorption cycle, capable to be thermally cycled at rapid rates, in order to process reasonable hydrogen flow rates. Each type of reactor combines the effective increase of the thermal conductivity, optimized solutions to dissipate more effectively the heat of reaction and the good permeability to hydrogen gas. The FMHR, with the characteristics presented in figure 3, have the same active volume, capable to accommodate 120 g of hydride alloy powder.
The experimental set-up shown in figure 4 is designed to provide thermal absorption-desorption cycles for the FMHR and a Data Logger measure the main parameters of the process [5].

The thermal cycling experiments were focused on the study of the parameters which affect the FMHR performances: (i) operating parameters as cooling and heating water flow rate and temperature, (ii) overall heat transfer coefficient improved by conducting additives added to MH, (iii) metal hydride bed thickness and (iv) the increment of heat exchange surface reactor.

The absorption and desorption duration were chosen to allow almost complete reaction according to p-c-T curves of LaNi₅.

Applying this strategy, the experiment has been made following three main directions:

(i) In parallel, two FMHR type I were filled, one with 120 g LaNi₅ and the other with a mixture 120g LaNi₅ plus 5.25 g of our conducting additive (CA) were tested by varying operating parameters regarding temperature and flow rate of cooling and heating fluids;

(ii) Four type II FMHR were filled, one with 120 g LaNi₅ and for the others three adding to hydrogen storage powdered alloy an amount of some different conductive additives (CA based on carbon, adsorbent carbon and graphite) to increase the effective thermal conductivity of the bed, and cycled with different operating parameters to determinate their cycling behaviour;

(iii) FMHR type III and FMHR type IV with increased heat exchange surface, filled with the same quantity of mixture LaNi₅ + CA, having the bed alloy thickness $\Delta_{\text{bed}_{\text{III}}}=4\text{mm}$ and $\Delta_{\text{bed}_{\text{IV}}}=2.5\text{mm}$ were tested about 3000 absorption-desorption cycles varying the cycle duration.

3. Results and discussion

Figure 5 shows the time dependence of hydrogen absorption capacity of FMHR type I on the flow rate of cold fluid at a given absorption temperature $T_L=20^\circ\text{C}$. It is observed that the duration of a full hydrogen absorption cycle decrease for high flow rates.

Figure 6 shows that that for a given supply pressure, hydrogen delivery and storage pressure increases with the hot fluid temperature, due to the increase in equilibrium pressure of the hydride bed with bed temperature according to van’t Hoff equation. Thus, all later experiments were performed in the temperature range 20-80°C, using 12 l/min cold-hot water flow rate.
Reactor I. Absorption at different cooling water flow rates $Q_{\text{des}}$; $T_{\text{L}}=20^\circ\text{C}$; $P_{\text{abs}}=8$ bar

Reactor I. Desorption at different heating temperatures $T_{\text{H}}$; $Q_{\text{des}}=12$ l/min

Reactor II. Absorption-Desorption cycle Mixture (MHx+CA) versus MHx $T_{\text{L}}=20^\circ\text{C}$; $T_{\text{H}}=80^\circ\text{C}$; $Q=12$ l/min; $P_{\text{abs}}=8$ bar; $\Delta_{\text{bed}}=4$ mm

Reactor III vs Reactor IV. Absorption-Desorption cycle material: 125 g LaNi$_5$+CA; $\Delta_{\text{bed}}=4$ mm; $\Delta_{\text{bed}}=2.5$ mm

Figure 5. Variation of absorption cycle with cold fluid flow rate.

Figure 6. Variation of pressure and hydrogen desorption with fluid temperature.

Figure 7 shows the effect of CA conducting additive mixed with metal hydride on the duration of absorption-desorption cycle due to the increased effective thermal conductivity of the alloy bed. It was found that an amount of 4.3% conductive additive added to the LaNi$_5$ alloy does not affect the hydrogen absorption rates, but increases the reaction kinetics and could reach the target of 120 seconds cycle life.

Figure 8 shows the superior behavior of our CA conductive additive versus other carbon based additives like adsorbent carbon and graphite.

Figure 9 shows the influence of bed design and heat exchange unit optimization on the dynamic characteristics of FMHR. It is observed that a smaller bed thickness and an extended heat exchange surface of metal hydride reactor type IV increase the reaction kinetics.

Reactor IV Absorption-Desorption short cycle Mixture (MHx+CA) versus MHx

Figure 7. Effect of CA about the duration of a cycle.

Figure 8. Behavior of some additives in LaNi$_5$.

Figure 9. The influence of reactor bed design.

Figure 10. Similitude of two thermal cycle.
Thermal cycles of a FMHR type IV, shown in figure 10 using as hydriding materials LaNi$_5$ and (LaNi$_5$+CA) mixture, show that the reactor can be cycled at a rapid rate of 120 seconds providing a good hydrogen absorption capacity of 0.85% H-weight, and a satisfactory flow rate, 10 N liters/cycle.

4. Conclusions
The design and development of fast metal hydrides reactors has been studied, for an investigation of the coupled heat and mass transfer process that take place in hydrogen storage/compression devices. Dynamic characteristics of the developed FMHR define that the absorption/desorption cycle duration is improved using our novel mixture metal hydride-CA conductive additive due to the increased effective thermal conductivity of the alloy bed. The advanced hydride bed design with high heat transfer capabilities can be thermally cycled at a rapid rate, under 120 seconds, in order to process high hydrogen flow rates.

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