

Low cost and compact continuous hydride cycling system

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The study and characterization of new materials for use in hydrogen storage includes knowing their performance, stability, aging and degradation resulting from charge-discharge cycles. With this objective in mind, our group has developed an automated device whose purpose is to repeatedly undergo hydrogen charging and discharging in order to assess the longevity of the hydride. Besides fast cycling to saturation of the hydride up to a maximum pressure of 20 bar, the apparatus is also able to measure detailed isothermal charging curves at different temperatures between 10°C and 230°C. The system is compact enough to allow its use on different locations and permits the interchangeability of the connected sample chamber to use its cycling ability to assist the use of other equipment. The equipment was tested with the LaNi₅-H system, where a known significant degradation is observed over 1500 cycles.

I. INTRODUCTION

The use of renewable energy sources is growing continuously nowadays, forcing the adaptation of technologies related to energy production, transport and storage. Hydrogen fits specially in this development as a valuable energy vector if it can be efficiently produced close to the primary power source and conveniently stored and transported for later use, e.g., as fuel in electric vehicles or in stationary applications powered by fuel cells.¹⁻³ However, the acceptability and success of hydrogen as a competitive alternative to the presently used techniques of storing energy is still dependent of the development of many associated technologies like the storage of hydrogen.⁴⁻⁶ Although much of the current effort within this field is focused in the US Department of Energy targets for automotive applications of hydrogen and thus the search for adequate lighter materials for its storage, size and weight of storage facilities are not a problem in stationary applications such as in micro generation systems, where energy storage is a major step towards energy autonomy. The use of metals and metallic alloys for hydrogen storage is then a reasonable option, as they are known and studied for decades and high efficiency and high capacity alloys can be produced.

The optimization of storage in solid materials requires the study of their properties and behavior upon absorption of hydrogen. One of the issues pertinent to the optimization of metal hydride storage tanks is related to the degradation of the hydriding properties of the alloy with aging due the repeated charge and discharge cycling processes. The changes of the crystalline lattice parameters when absorbing hydrogen are responsible

for the brittleness of the material and reduction of the size of the grains constituting the hydride bed, eventually leading to the degradation of their surface and bulk properties related to the ability of dissociating the hydrogen molecule and to incorporate the hydrogen atoms into its crystalline structure. This affects the useful life-time of the hydride bed, by affecting the main properties needed for an efficient storage of hydrogen, namely the maximum capacity of absorption and shape and pressure of the plateaus of isothermal charge and discharge pressure vs. concentration curves.

The characterization of the hydrogen absorption properties of new materials for hydrogen storage is typically performed with high accuracy Sieverts-type volumetric devices.⁷ Studying the aging of hydrides requires taking a sample through many hydriding cycles.⁸ This task, however, does not need the high level of accuracy of costly conventional equipment. Many authors present results of cycling in automated systems⁹⁻¹² and some report the use of systems dedicated to other specific tasks also needing cycling¹³⁻¹⁵, but all of those are not efficient for the specific task of extensive cycling. Meyer, et al.¹⁶ presented a similar system dedicated solely to cycling. In this paper, we present a different dedicated Sieverts-type volumetric device that allows repeated automated cycling of hydrogen absorption and desorption over a non-limited number of cycles, built with a compact and simple structure based on two reference volumes, which gives it a great versatility of use and the possibility of reusing the hydrogen by circulating it through the linear sequence of volumes of the system.

In this paper, we start by presenting the layout of the compact apparatus, based on low cost and interchangeable parts. We then present the possible modes of operation, showing its versatility. Its compactness makes it portable enough to allow its use in other applications outside the home laboratory. In the last section, we present an example of application in the study of the reference hydride of the intermetallic alloy LaNi_5 .

II. EXPERIMENTAL APPARATUS AND METHODS

A. General description

The diagram of Fig. 1 shows the assembled equipment, which is based on a volumetric Sieverts-type system^{7,17} built with purchased elements from Swagelok Ltd, Keller Ltd. pressure transducers, and electro-valves from ASCO Numatics Ltd. The core of the pressure cycling system is composed of three volumes separated by electro valves that allow the successive expansion of known amounts of hydrogen gas from a first reference calibrated volume V_{ref1} to the sample chamber during the charging process and from the sample chamber to a second reference calibrated volume V_{ref2} in the discharge process. The auxiliary volume is part of the reference

volume V_{ref1} and can be extended or substituted to the best accommodation of the relation between reference volume and dead volume in the chamber. The same is possible in V_{ref2} if needed to adequate the aliquots of expanding gas from the sample chamber in desorption conditions. The system was designed to hold pressures of up to 20 bar. The expansions of gas are made the valves identified in Figure 1 in the usual way on volumetric systems, with the amount of admitted or released gas from the chamber always accounted for. Pressure is measured on the two reference volumes with the transducers identified as P1 and P2 in the diagram of Figure 1. The pressure variations in relation to the volume ratios are used for the calculations of the absorbed gas at the points of equilibrium when closing one of the valves of the chamber.

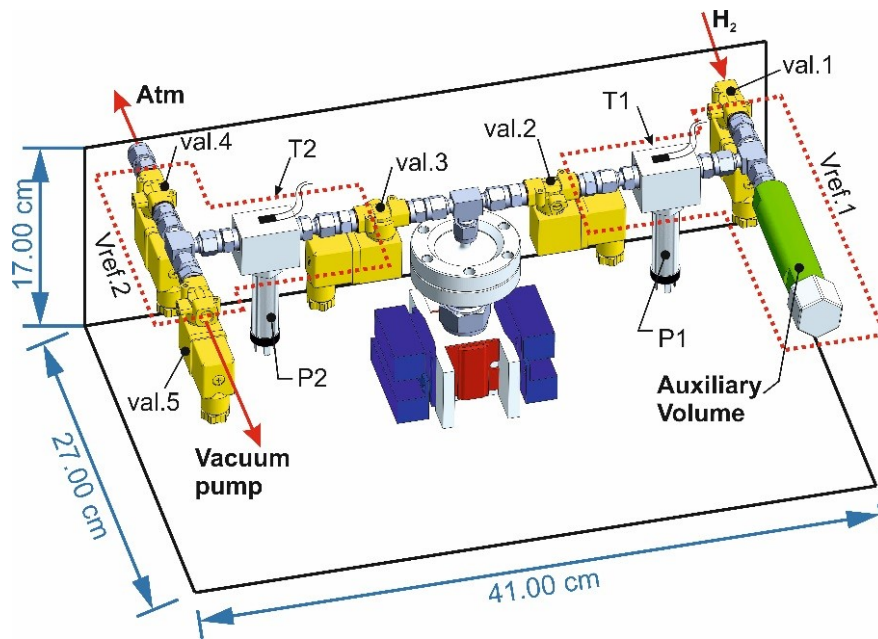


FIG. 1: Schematic diagram of the volumetric system with the temperature controlled sample chamber. The dotted lines delimit the two reference volumes.

A rotary vacuum pump ($< 10^{-1}$ mbar) uses the dedicated port on valve 5. The control of the automatic operation is based partly on the measurements of pressure. The measurement of temperature is made in three points, with one PT100 on each reference volume, identified as T1 and T2 in the diagram of Figure 1, and a third one in the body of the sample chamber. The reference volumes were calibrated by repeated expansions of hydrogen from a previously calibrated volume in our main Sieverts-type apparatus to the evacuated volumes.

In its current layout, our system relies on a bottle of compressed pure gas as source of hydrogen and liberates the used gas to the atmosphere in safety conditions through valve 3 or through the vacuum pump on valve 5. However, the two volumes design and the use of unidirectional valves make the system more versatile than the usual Sieverts apparatuses, allowing a simple cycling of the used gas if a dry compressor and a purifying filter are added to the system between valves 1 and 4.

This low-cost system is also very compact. As it is mounted on a small rigid rig, it can be transported to other locations with minor rearrangements of ancillary equipment.

B. Sample chamber

The sample chamber is designed to have a minimum dead volume possible and to place the sample in the center of the temperature controlling devices, as shown in Fig. 2. The body of the chamber is made of aluminum to ensure a good thermal conduction. A thermal control block, also made of aluminum, is attached to the external surface of the chamber, with a height ensuring the best conditions of temperature homogeneity of the small volume reserved for the sample (0.785 cm^3). Two heaters are mounted on opposed external surfaces of the thermal block. Two Peltier units are mounted on the other two opposing surfaces of the block with ventilated heat-sinks on the external hot surfaces. The temperature of the sample is monitored by the PT100 mounted inside the body of the sample chamber on a thin hole, with its measuring tip at a distance of 5 mm from the sample. The temperature of the sample can thus be controlled in the range from $10 \text{ }^{\circ}\text{C}$ to $230 \text{ }^{\circ}\text{C}$ without damaging the constituent parts of the chamber.

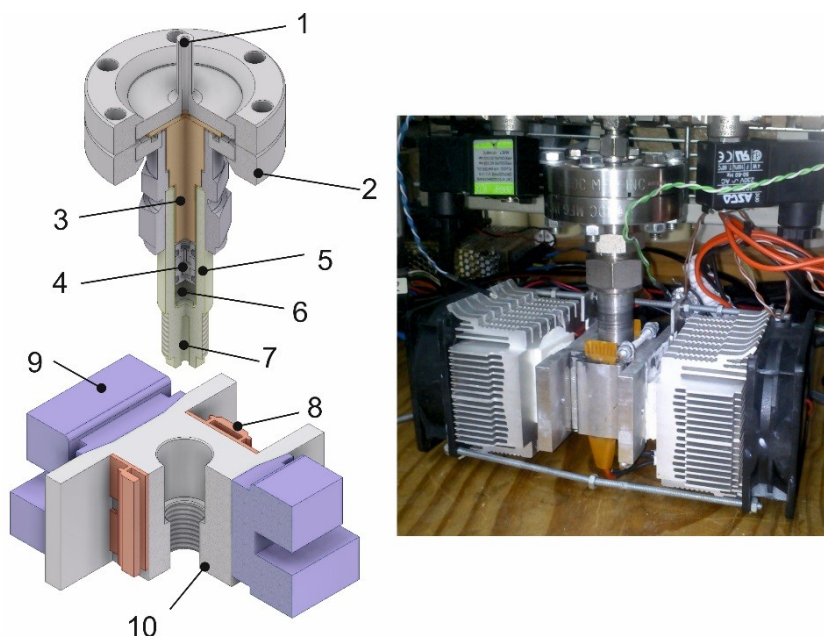


FIG. 2: Sample chamber and thermal control: (1) Gas port; (2) Flange DN40CF 70mm OD closing the chamber; (3) Stainless steel part reducing the internal free volume; (4) Quartz wool encapsulated filter; (5) Aluminum sample container; (6) Sample space with 0.785 cm^3 ; (7) Temperature sensor; (8) Resistive heater; (9) Cooling Peltier element and heat sink; (10) Aluminum heat coupling block.

The sample chamber is attached to the base system through a DN40CF 70 mm OD flange sealed with a copper ring. This flange allows the alternative attachment of other devices that need a basis for measuring hydrogen absorption and control of many hydriding successive cycles. One of such attachments in our lab is a capacitive chamber for measurement of hydride volume changes.¹⁸ A second device is an operational high-pressure (10 bar) chamber for *in-situ* X-ray powder diffraction measurements, attachable through a long thin tube to allow its insertion in the X-ray diffractometer. The portability of the device is here very important.

C. Control and automation

The experiment is controlled from a desktop computer through a code developed in LabView with a graphical interface. The sequence of valves opening and closing, the number and type of cycles and the operation temperature are defined in the graphical interface. From the start of the defined sequence, the temperature, pressure and status data are constantly monitored and their values are registered at a chosen time rate in the computer for later analysis. A PID code was added to the controlling code for the thermal control.

A dedicated control and communication board was developed for the automation of this equipment. The board was built with the following components: a 16 bits microcontroller (MSP430F249TPM - Texas Instruments) for the management of internal functions; a set of solid state relays (AQG22105 Panasonic Industrial Devices) to actuate the electro-valves and the heating resistances; MOSFETS to actuate the Peltier elements; a 24 bits Analog to Digital Converter (ADS1248IPW - Texas Instruments) for the reading of the three temperature probes, the two pressure transducers, and the vacuum gauge installed between the vacuum pump and valve 5; an RS-232 port (MAX3221EIPWG4 - Texas Instruments) as interface with the controlling computer. Through a small keyboard attached to the main control board it is also possible to control the valves opening and closing manually.

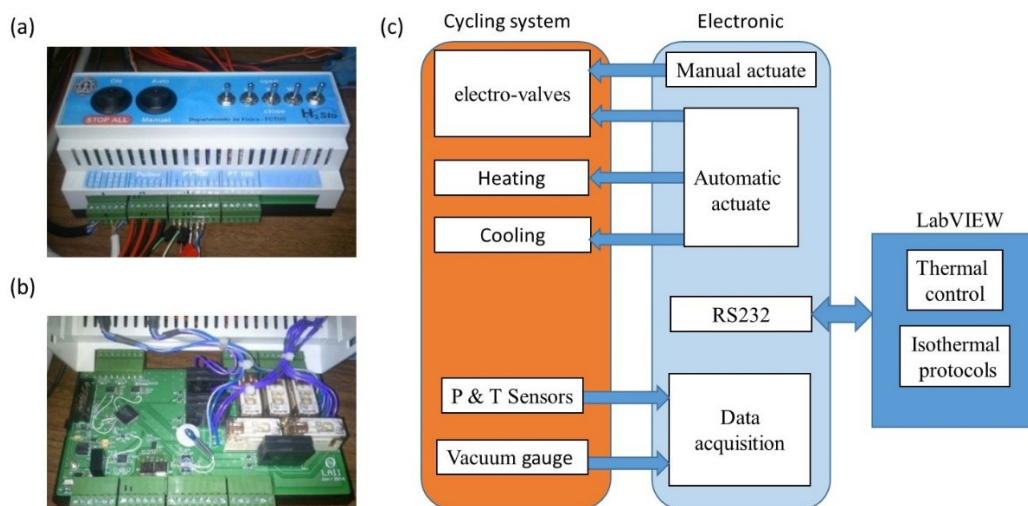


FIG. 3: (a) Manual control keyboard; (b) Electronic control board; (c) Actuation diagram of the cycling system.

With this controlling code and board, we can perform different types of operation with the system: a) simple monitoring of the absorption capacity with fast gas absorption using single large aliquots on each cycle with a starting high pressure of up to 20 bar and evacuation at the end of the cycle; b) slow isotherms of absorption and desorption with choice of the number of steps or equilibrium pressures and with the choice of waiting for pressure equilibrium through monitoring the pressure time variations; c) measurement of isotherms or cycling with the sample at different temperatures within the operating range (10-230°C).

III. EXAMPLE OF APPLICATION WITH THE REFERENCE HYDRIDE OF LaNi_5

As an example of application of this cycling device, we present results of hydriding cycling of a sample with 0.9206 g of mass of the known reference hydride of the intermetallic AB₅ compound LaNi_5 , purchased from Alfa Aesar (99.9%, REO).

We performed 1500 fast hydriding cycles, interrupted at cycles 5, 500, 1000 and 1500 to perform detailed isotherm absorption curves. Figure 4a shows the pressure variations on the last 50 cycles. Each cycle was initiated with a pressure of 12 bar on the reference volume V_{ref1} and the charge was performed on one single expansion, with saturation reached at around 4 bar, above the plateau pressure at room temperature, as depicted in Figure 4b for five successive cycles. Desorption processes were performed by rapid expansions to the second reference volume V_{ref2} until a low enough pressure was achieved to evacuate the chamber. The temperature of the sample chamber was continuously monitoring, showing an increase on each absorption part due to the exothermal absorption reaction (Fig. 4b). On desorption no variation in temperature was observed, as a larger number of expansion steps are used.

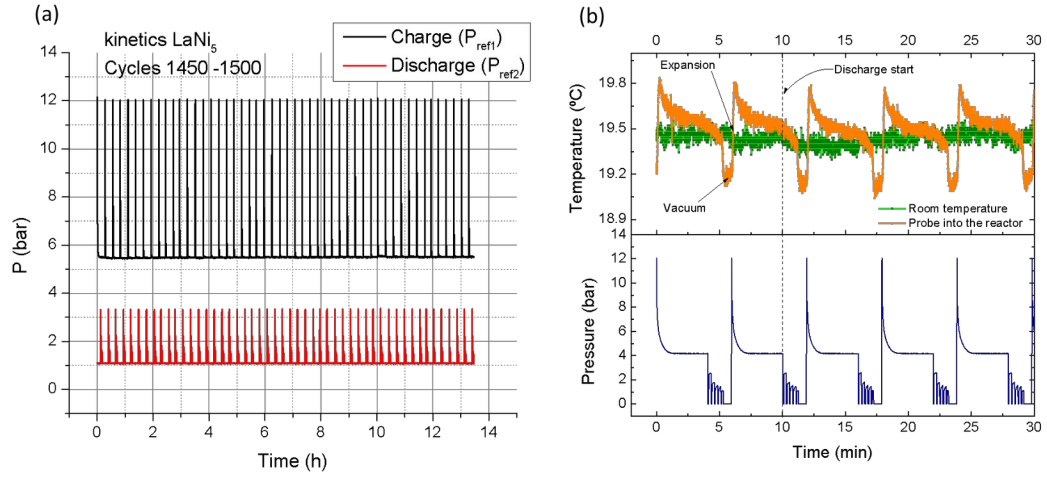


FIG. 4: a) Partial view of the pressure vs. time cycling of LaNi_5 ; b) Detail of hydriding/dehydriding cycles.

One important parameter relevant to the degradation of hydriding properties of an intermetallic compound is related to the loss of capacity for absorption along the cycling. Figure 5a) shows the measured capacity, as the maximum concentration achieved on each fast cycle of the present assay. The observed degradation is known to be originated in the disproportionation phenomenon that deteriorates the very composition of the surface of the grains of the powdered alloy, reducing the total volume actually absorbing hydrogen.^{19,20}

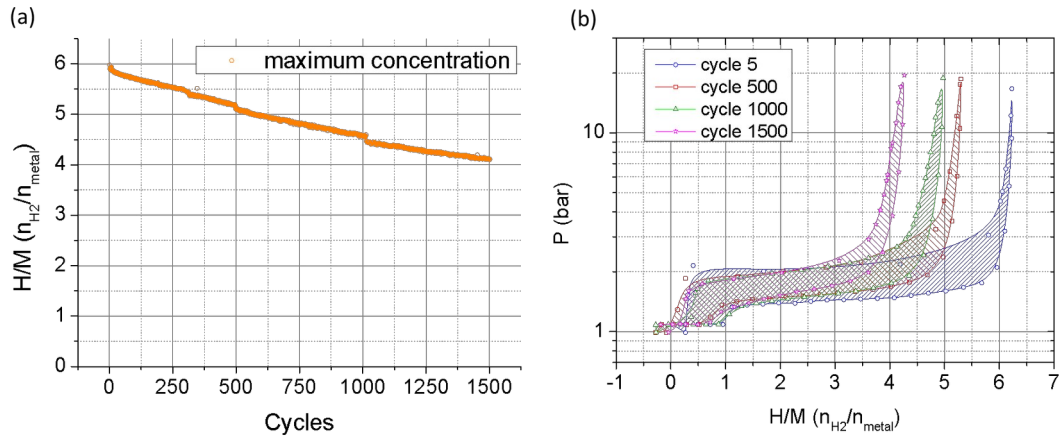


FIG. 5: (a) Hydrogen absorption capacity as a function of the number of pressure cycles for LaNi_5 . (b) Isothermal room temperature isotherm curves acquired at different points during the cycling process.

One other important parameter relevant to the degradation of hydriding properties of an intermetallic compound is related to the changes in the shape of the absorption / desorption isotherm curves. This system allows the measurement of isotherms at any given point of the cycling procedure: an absorption isotherm is obtained by allowing smaller amounts of gas to expand from the first reference volume to the sample chamber and successively increase the equilibrium pressure, while a desorption curve is obtained by expanding from the

sample chamber to the second reference volume in successively lower equilibrium pressure steps. On the present application example, we performed room temperature isotherm measurements of pressure vs. hydrogen concentration on the cycles no. 5, 500, 1000 and 1500, as shown in Figure 5b). Along with the obvious decrease of the maximum concentration achieved, we also see the change of the slope of the plateau originated by the degradation of the homogeneity of composition of the alloy.

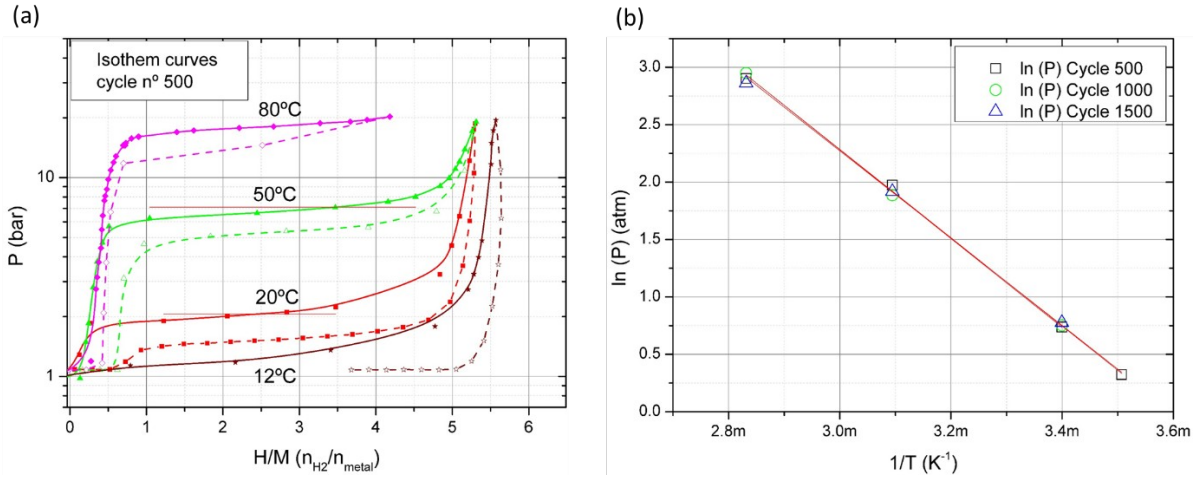


FIG. 6: A series of isotherm P (H/M) measurements at different temperatures for LaNi₅ acquired at cycles 500- 503 (a), and the respective van't Hoff plot (b).

On the occasions where the sequence of rapid absorption / desorption cycles was interrupted, around cycles 500, 1000 and 1500, we also measured isotherm curves acquired at different sample temperatures, as shown in Figure 6a) for cycles 500-503. The respective van't Hoff plot of the logarithm of the absorption mid-plateau pressure vs. inverse temperature is shown in Figure 6b). The values of the thermodynamic parameters of the hydrogen dissociation and absorption reaction are derived from the van't Hoff equation:

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

We measured on the three points of the cycling the same values of $\Delta H = -32$ kJ/mol and $\Delta S = -115$ J/(K mol) known for LaNi₅H_x.

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REFERENCES

- ¹G. Zini and A. D. Rosa, "Hydrogen systems for large-scale photovoltaic plants: Simulation with forecast and real production data," *International Journal of Hydrogen Energy* 39(1), 107–118 (2014).
- ²E. L. González, F. I. Llerena, M. S. Pérez, F. R. Iglesias and J. G. Macho, "Energy evaluation of a solar hydrogen storage facility: Comparison with other electrical energy storage technologies," *International Journal of Hydrogen Energy* 40(15) 5518–5525 (2015).
- ³D. Mori and . K. Hirose, "Recent challenges of hydrogen storage technologies for fuel cell vehicles," *International Journal of Hydrogen Energy* 34 (10) 4569–4574 (2009).
- ⁴E. Martin, S. A. Shaheen, T. E. Lipman and J. R. Lidicker, "Behavioral response to hydrogen fuel cell vehicles and refueling: Results of California drive clinics," *International Journal of Hydrogen Energy* 34(20) 8670–8680 (2009).
- ⁵G. Frenette and D. Forthoffer, "Economic & commercial viability of hydrogen fuel cell vehicles from an automotive manufacturer perspective," *International Journal of Hydrogen Energy* 34(9) 3578–3588 (2009).
- ⁶M. Ball and M. Weeda, "The hydrogen economy – Vision or reality?," *International Journal of Hydrogen Energy* 40(25) 7903–7919 (2015).
- ⁷D. Broom, "The accuracy of hydrogen sorption measurements on potential storage materials," *International Journal of Hydrogen Energy* 32(18) 4871–4888 (2007).
- ⁸S. W. Lambert, D. Chandra, W. N. Cathey, F. E. Lynch and R. C. B. Jr., "Investigation of hydriding properties of LaNi_{4.8}Sn_{0.2}, LaNi_{4.27}Sn_{0.24} and La_{0.9}Gd_{0.1}Ni₅ after thermal cycling and aging," *Journal of Alloys and Compounds* 187(1) 113–135 (1992).
- ⁹H. Cheng, X. Deng, S. Li, W. Chen, D. Chen and K. Yang, "Design of PC based high pressure hydrogen absorption/desorption apparatus," *International Journal of Hydrogen Energy* 32, 3046 – 3053 (2007).
- ¹⁰S. Li, W. Chen, G. Luo, X. Han, D. Chen, K. Yang and W. Chen, "Effect of hydrogen absorption/desorption cycling on hydrogen storage properties of a LaNi_{3.8}Al_{1.0}Mn_{0.2} alloy," *International Journal of Hydrogen Energy* 37(4) 268–3275 (2012).
- ¹¹F. Laurencelle, Z. Dehouche and J. Goyette, "Hydrogen sorption cycling performance of LaNi_{4.8}Sn_{0.2}," *Journal of Alloys and Compounds* 424(1–2) 266–271 (2006).

- ¹²F. Qin, L. Guo, J. Chen and Z. Chen, "Pulverization, expansion of La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2} during hydrogen absorption–desorption cycles and their influences in thin-wall reactors," *International Journal of Hydrogen Energy* 33(2) 709–717 (2008).
- ¹³B. Charlas, O. Gillia, P. Doremus and D. Imbault, "Experimental investigation of the swelling/shrinkage of a hydride bed in a cell during hydrogen absorption/desorption cycles," *International Journal of Hydrogen Energy* 37(21) 16031–16041 (2012).
- ¹⁴B. Charlas, A. Chaise, O. Gillia, P. Doremus and D. Imbault, "Investigation of hydride powder bed swelling and shrinking during hydrogen absorption/desorption cycles under different compressive stresses," *Journal of Alloys and Compounds* 580, S149–S152 (2013).
- ¹⁵M. Matsushita, M. Monde and Y. Mitsutake, "Experimental formula for estimating porosity in a metal hydride packed bed," *International Journal of Hydrogen Energy* 38(17) 7056–7064 (2013).
- ¹⁶G. Meyer, P. A. Larochette, A. Baruj, F. J. Castro, P. Lacharmoise, E. Zacur and B. A. Talagañis, "Equipment for hydrogen absorption-desorption cycling characterization of hydride forming materials.," *Rev. Sci. Instrum.* 78(2) 023903 (2007).
- ¹⁷T. Blach and E. Gray, "Sieverts apparatus and methodology for accurate determination of hydrogen uptake by light-atom hosts," *Journal of Alloys and Compounds* 446–447, 692–697 (2007).
- ¹⁸E. S. Ribeiro and J. M. Gil, "A novel capacitive device for the study of volumetric expansion of hydride powders," *International Journal of Hydrogen Energy*, *in press*. <http://dx.doi.org/10.1016/j.ijhydene.2015.08.063>
- ¹⁹J. I. Han and J.-Y. Lee, "An investigation of the intrinsic degradation mechanism of LaNi₅ by thermal desorption technique," *International Journal of Hydrogen Energy* 13(9) 577–581 (1988).
- ²⁰P. Goodell, "Stability of rechargeable hydriding alloys during extended cycling," *Journal of the Less Common Metals*, vol. 99(1) 1-14 (1984).