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Instrumentation and characterization of materials for hydrogen storage

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Abstract

In order to identify and follow the challenges in the use of materials with the capacity to absorb hydrogen for energy storage, many groups address a diversity of issues, where the need to study the properties of the material upon absorbing hydrogen is always present. Appropriate equipment and techniques are needed: besides the use of classical systems, many research groups identified recently the need to study in more detail the properties related to the macroscopic changes of volume of the hydride powder as hydrogen content is cycled. In this article, we present the equipment and techniques developed by our group: after the classical volumetric systems, we addressed the problem of volumetric changes by building a novel coaxial capacitive system. This system measures the volume and porosity of a small amount of free hydride powder as a function of hydrogen content, after applying a complex deconvolution algorithm on the primary AC electric measurements.

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1. Introduction

Hydrogen is recognized as an excellent means of carbon-free high-density energy storage with well-identified potential applications in energy technologies when integrated with renewable resources at various scales of size and geographic distribution. Government agencies recognize the importance of hydrogen in this context, e.g. by defining related clear objectives within the current European Program Horizon 2020 [1,2].

Hydrogen can be produced by electrolysis using renewable primary sources [3, 4]; it can then be stored for later use in fuel cells, where the only generated residue is water. It can also be the fuel of internal combustion or turbine engines [5]. When burned in a pure oxygen environment, the only products are heat and water. Burning hydrogen in the atmosphere forms

some nitrogen oxides. Still, the burning of hydrogen produces fewer pollutants than fossil fuels. If applied in the automotive sector, it would change the landscape of greenhouse gas emissions, especially in urban areas.

Among the challenges in the introduction of hydrogen as an energy vector, a key point is the development of efficient and safe storage means and the related technologies [3,5]. Hydrogen can be stored as a gas, liquid or in solid medium. The latter method best meets safety and volumetric energy density requirements. Nevertheless, storage in solid has several limiting important issues that must be resolved before its application, such as changes in the powder bed morphology (volume, grain size, compaction, and agglomeration) and chemical and kinetic degradations as hydrogen is cycled.

Many solid media have been explored in the search for high-capacity or high-density hydrogen storage, from intermetallic compounds of various structures to lighter materials, such as carbon nanostructures or microporous materials, zeolites and MOFs [3,4]. Composites that cross those materials groups have

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also been suggested to facilitate adsorption mechanisms and control the thermodynamics of adsorption and desorption [6].

The introduction of hydrogen atoms in the lattice of solid materials like in the formation of metal hydrides, or the adsorption of molecular hydrogen in porous materials, leads to structural deformations causing a reversible expansion of the lattice volume. This variation at the atomic level can be converted into large macroscopic changes, which can reach up to ~30% in metal hydrides, causing severe problems, from stresses on the walls of containers to the reduction of the gas flow, potentially compromising the integrity and efficiency of containment tanks. Successive cyclic changes of crystal lattice volume lead to embrittlement of the storage material and therefore its degradation, and in some cases the reduction of grain sizes. The hydride formation reaction may be highly exothermic, while the discharge process is endothermic. Therefore, it is always necessary to consider the thermal control for optimization of the hydrogen reversible storage capacity of the systems. These and other challenges must be addressed with a better understanding of material properties and a more careful characterization so that hydrogen storage units can be included more efficiently in integrated systems for energy storage.

Previous studies of the expansion effects have used direct observations in transparent chambers or complex methods such as neutron tomography [7,8].

In a recent investigation, we pioneered an alternative method to observe variations in the morphological properties of powders for hydrogen storage by means of electrical measurements (resistance and capacitance measured in AC with a fixed frequency). This work demonstrated the possibility to evaluate, *in-situ*, volumetric expansion, porosity and packing density of hydrogen storage materials with a great precision derived from sensitive electrical capacitance variations [9,10].

In this article, we describe the techniques developed and systems mounted at the Laboratory for Hydrogen of the Physics Department of the University of Coimbra, which encompass the capacitive chamber for measurements of macroscopic volume changes, one chamber for *in-situ* X-ray powder diffraction measurements, and two fully automated Sieverts apparatus, one of them used for high precision hydrogen content measurements as a function of gas phase pressure and temperature, and the second for evaluation of changes of hydride performance through a high number of charge cycles.

2. Experimental techniques and equipment

For the best development of technologies related to the integration of hydrogen in renewable energies, it is necessary to better understand the intrinsic properties of the material. Preferably, the characterization of the materials for hydrogen storage must be done *in situ*, or in conditions similar to the end use of these materials, namely as a function of hydrogen content and temperature.

Looking to meet these requirements we have developed a series of experimental systems and routines for better characterization of the materials, with the aim of identifying the behaviour of the material as it reacts with hydrogen under the same conditions as the end use.

2.1. Measurement of hydriding properties

The volumetric measurement method for the study of hydrogen storage, also known as Sieverts method named after the German chemist Adolf Ferdinand Sieverts, uses temperature and pressure direct measurements, and an appropriate equation of state (EOS) of the gas to calculate the amount of H₂ present in the gas phase inside the calibrated volumes of the system. In a typical measurement, the gas expands at successively increasing pressures from a reference volume to the chamber containing the sample under study; the absorbed (or adsorbed) quantity of hydrogen is revealed as a pressure drop from what is expected solely from the EOS and the known volumes and temperature. If the absorption is not too fast, the kinetics of absorption can also be followed by recording the measured parameters as a function of time.

Our main Sieverts system is schematically presented in Fig. 1 and consists basically of tubing and fittings of 316 stainless steel and four pneumatic NOVASWISS valves. It was designed to work at high pressure, limited by the range (0–100 bar) of the pressure piezoresistive transducer (KISTLER 4045 A100 – P100 in Fig. 1). A second, 0–5 bar range transducer may be used (P5 in Fig. 1), by opening a manual valve mounted between both transducers for the protection of P5 when working at higher pressures. The pressure transducers are mounted directly in the reference volume, marked by a dashed line (yellow on-line) in Fig. 1, composed of tubing and fittings between valves. This reference volume is ideally of the same magnitude as the free volume (gas phase) in the sample chamber to achieve the best resolution of

the system. Therefore, expansion volumes of different sizes were programmed to be attached to the reference volume through yet another auxiliary manual valve, effectively increasing the reference volume when needed. A third auxiliary manual valve serves to connect the system to other equipment, when needed.

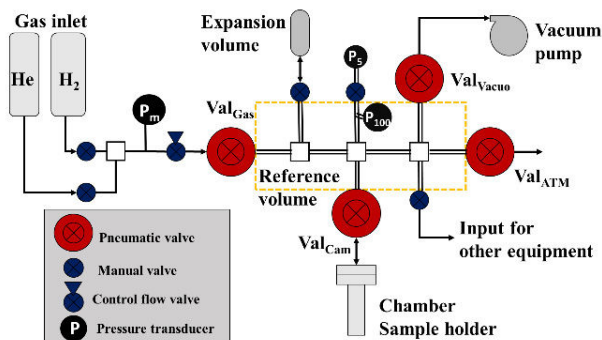


Fig. 1. Diagram of the pneumatic volumetric Sieverts system. The dashed line (yellow on-line) highlights the reference volume.

The Sieverts system is controlled by a NI-DAQ PCI-MIO-16XE-50 (resolution of 16 bits and accuracy of 1,443 mV), which makes the acquisition of pressure and temperature data and allows the control of the valves through a graphical user interface developed in LabVIEW.

The operation of the pneumatic valves is performed with compressed air at 6.9 bar, actuated through ASCO solenoid pilot valves. The automatic operation of the system is performed through the actuation of the four pneumatic valves in pre-defined sequences, assisted by decision algorithms based on calculations of pressure time variations. Valve Val_{gas} is the inlet for the gas. The device has two gas inlets with manual valves for the selection of the gas to be used in the study. Before the reference volume there is a mechanical pressure gauge P_m to monitor the pressure in the hose before entry into the system, which is made through a flow control Swagelok SS-31RS4-G valve. For the best operation of the automation equipment, the flow control valve must be adjusted to a slow flow according to the absorption kinetics of the test sample. The second pneumatic valve Val_{Atm} is used to reduce the pressure in the reference volume to atmospheric pressure by releasing the gas to the atmosphere external to the lab. The third pneumatic valve Val_{Vac} connects the reference volume to a vacuum pump capable of reducing the pressure to a value below the accuracy limit of the piezoresistive pressure transducers.

The fourth pneumatic valve Val_{Sample} makes the connection between the reference volume and the sample chamber, allowing the expansions needed in the sequences to obtain isothermal Pressure-Concentration curves that characterize the hydrogen absorption capacity of a material, or to study the kinetics of absorption or desorption.

To ensure the best operation of the equipment in the study of materials with low absorption capacity, it is essential to test and eradicate external and internal leaks of the system and its valves. Vacuum holding tests are the first approach. Then, an inert gas like He is used in high-pressure tests, eventually using a He leak detector and later monitoring eventual pressure drops during long periods (up to 24 h). We later assembled a low-cost hydrogen sensor (MQ-8 Hanwei Electronics Co., Ltd, capable of detecting concentrations in the range of 100 to 10000ppm), which proved to be very efficient in detecting local micro-leaks, although time-consuming, if positioned next to any suspected point and covered with aluminium foil for a few minutes to allow the accumulation of gas leaking from the pressurized system to the outside.

Volumetric systems rely on knowledge, with great precision, of the volumes involved, in particular the reference volume and the volume of the sample chamber or reactor. The primary calibration of volumes is performed by expanding a known gas from a calibrated diameter glass tube to the previously evacuated volume to be measured. The gas in the tube is separated from outside air by a plunger moving freely inside the vertical tube, sealed by a mercury ring. The gas pressure is constant throughout the procedure, slightly higher than one atmosphere (adding the plunger's weight). During the expansion, the plunger moves down inside the tube with a displacement that is directly proportional to the volume under measurement. After a few hundreds of such measurements, we accumulate enough statistics to attain a high precision in the value of the measured volume: the main reference volume of our system is $7.428(9) \text{ cm}^3$.

Another condition for a good performance of a Sieverts apparatus is the control and measurement of temperature. The room temperature in our lab is air-conditioned and continuously measured and recorded when in operation, using a NTC thermistor attached to the reference volume and a thermocouple in the environment of the sample chamber, which is enclosed in a Venticell oven (MMM Medcenter Einrichtungen GmbH) when operating at temperatures between 10°C

above room temperature and 250°C. When different parts of the system are at different temperatures care must be taken to know the correct partition point of separation of the two temperatures that simulate the temperature gradient, which is achieved through a previous calibration [11]. This system is able to study the absorption or adsorption of any gas compatible with the materials of the tubing and valves, as e.g. CO₂, a very interesting application in studies of materials designed for the CO₂ arrest from the atmosphere [12]. In Fig. 2 we show some examples of test results of H₂ and CO₂ absorption by known porous materials obtained with our Sieverts system.

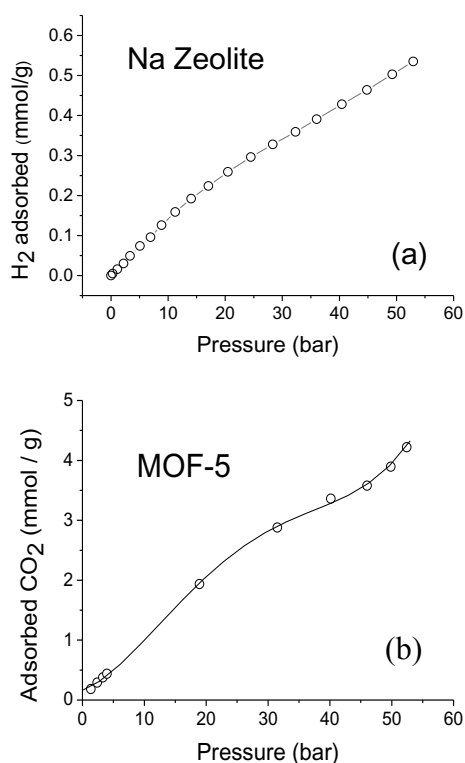


Fig. 2. Examples of adsorption test results using our Sieverts system. (a) High-pressure hydrogen adsorption at room temperature on Na-zeolite; (b) CO₂ adsorption isotherm at room temperature on MOF-5.

Regarding the hydriding properties of any material, another important parameter to study is the longevity (or aging) of its hydrogen charging capacity, thermodynamic properties, and kinetics of charging / discharging. A very large number of successive charge/discharge cycles, in the order of the thousands, are needed to have relevant information. Our pneumatic system is able to do this task in automatic

mode, but it turns out to be relatively slow due to the performance of the pneumatic valves, so that it would take too long for a single experiment, besides blocking the use of this high-accuracy system for other shorter tasks. Taking into account that this kind of study does not need the high precision of the pneumatic system, we developed a second Sieverts system using low cost but fast electromagnetic valves and lower precision pressure transducers. The automation routines can prepare a continuous cycling experiment for a number of fast cycles as large as needed, with eventual stops to measure isothermal curves at controlled temperatures from slightly below room temperature to about 120°C.

2.2. Measurement of hydride volume changes

In the storage of hydrogen by formation of metallic hydrides, the gas atoms dissolved in the lattice cause a deformation of the crystal lattice causing its expansion. In pure metals, the crystal lattice expansion is of the order of 20% [13]. In metallic alloys, deformation of the crystal lattice unit cell can vary from about 2 to 5 Å³ per atom of H [14]. The deformations of the crystal lattice by forming hydrides generate an increase in the gross volume of the material, i.e., the grains expand. However, the variation of the macroscopic volume of a certain volume of powder (hydride) is not directly derived from the variation of the grain size, since the volume of the spaces between grains also varies.

The volumetric changes of hydride powder beds within storage tanks are related to the shape, size, distribution of the particles within the container, and to the quantity of powder in each section of the container. If the grains are not allowed enough space to accommodate, the swelling during the hydrogenation process results in the material exerting stress on the walls of the tank in such a way that the structural integrity might be compromised [15]. A gas phase volume above the hydride bed (called dead volume) is normally used to contain the expansion of the hydride in order to minimize the stresses in the tank walls [16], but even so agglomeration and jamming effects may still cause stresses. While some approaches deal with flexible or porous structures to hold the hydride bed, the minimization of the dead volume is also an objective.

Therefore, the development of suitable tanks to meet the criteria in different sectors needs detailed knowledge of volumetric expansion of the materials with potential for efficient storage. Some properties

related to porosity and agglomeration need further study because they directly affect the longevity and structural integrity of the tanks.

Recently, some research groups have been reporting the study of volumetric changes of hydrides, also targeting other relevant aspects for the applications for hydrogen storage.

Neutron radiography images of a sample in a chamber allow the observation of changes of volume, porosity and density during charging and discharging of hydrogen [17,18].

Another experimental system for studying the macroscopic volumetric changes consists of a container with rigid walls, with the contained sample lightly pressed with a top loaded spring [19,20]. The volumetric changes are observed by means of the displacement of a piston at the top of the sample. With this device a volumetric decrease and porosity increase were observed in the course of hydrogenation cycles.

Porosity changes of the $\text{LaNi}_5\text{-H}_2$ system were studied by another group through direct observations of the variation in height of the hydride bed, in a transparent chamber [8].

Aware of the problems related to volumetric changes of the hydrides, we were already developing a system to study these properties when those groups started to publish their results. We started using a different technique, based on electrical capacity measurements, which revealed to be a powerful technique for the purpose, with still a lot more to be achieved [9].

We designed an experimental system consisting of a chamber for high pressure with a capacitive sample holder with a coaxial geometry, in which we evaluate the changes of the volume and porosity of the hydride bed during the hydrogenation cycles through AC measurements of the electrical capacity and resistance. The chamber, depicted in Fig. 3, was designed in AISI 316 steel, with the inner walls of the body finely polished in order to minimize adsorption of gas during the experiment.

A specificity of this chamber is the small maximum volume available for the sample, 447.89 mm^3 , which revealed itself as an advantage in the study of powders truly free of stresses. Once the sample holder is mounted in the chamber, the total free internal volume (gas) is approximately 19 cm^3 .

Through the electric contacts of the chamber, a measurement of the capacity and resistance of the entire device is acquired by using a Automatic RLC Meter (digimess® RLC300) in RC mode, with a voltage of 1V at a frequency of 1 kHz. The

measurement is made in remote mode with RS-232 communication with a controlling computer, using an algorithm written in Python. Since the electrodes of the sample holder are isolated, the chamber is connected to ground via the RLC300 equipment, preventing the appearance of parasitic signals.

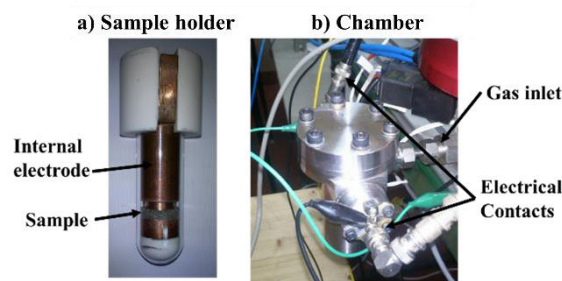


Fig. 3. Photograph of the capacitive volume expansion chamber: (a) Sample holder, composed of an internal electrode where the sample is mounted. The quartz tube involving the internal electrode is the primary dielectric of the coaxial capacitive chamber. (b) Vacuum and high-pressure tight whole chamber, with the gas inlet attached to the main Sieverts volumetric system. The electric contacts to the measuring RLC meter are highlighted.

Taking into account the geometry of the drawn sample holder as a coaxial capacitor, the electric signal composed of a pair of measurements (resistance and electric capacity) can be compared to an RC equivalent circuit model, so that we can obtain the parameters of physical interest (sample height and electrical resistivity) by means of a deconvolution algorithm. With the knowledge of the lattice parameters of the material under study and the variation of its hydrogen concentration we can also obtain the variation of the porosity. The lattice parameters may be acquired with the X-ray diffraction chamber built previously by our group for *in-situ* measurements under hydrogen pressure [21].

To show the sensitivity of this device, we illustrate in Fig. 4 the kinetics of activation of a pristine sample of the alloy LaNi_5 (Alfa Aesar GmbH & Co KG) as it started to absorb hydrogen in the first cycle. The capacitive dilation measurement chamber was mounted in the pneumatic Sieverts system in the place of a sample chamber to acquire the AC electrical signals simultaneously with the measurement of the concentration of hydrogen.

Fig. 4 shows the sample activation kinetics through the variation of pressure and hydrogen concentration, together with the measurements of the electrical capacitance and resistance. The sample had a mass of 0.60015 g. This sample shows a fast kinetics, due to the initially applied high pressure of over 20 bar.

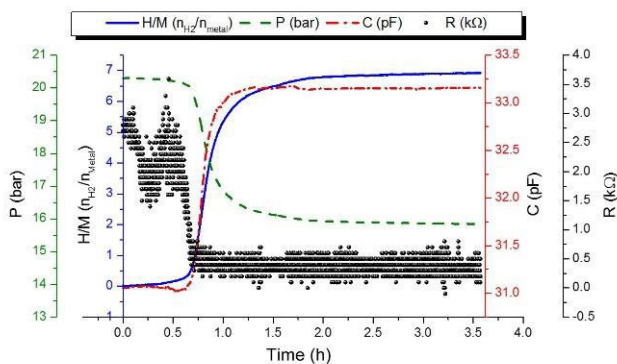


Fig. 4. Kinetics of activation for hydrogen absorption of a pristine LaNi_5 sample (0.60015 g) on the first absorption cycle, together with the respective electrical measurements performed in the capacitive volume expansion system.

The sample goes through an incubation period of about 45 minutes, after which the gas absorption accelerates to reach saturation.

In the first 30 min of the process we see a very smooth variation in pressure and electrical capacity and significant variations in the electrical resistance. During this time, the grains start to react with hydrogen in the chamber, initiating a fracturing process, but probably still maintaining its structure. This causes an initial high electrical resistance which oscillates within a range of about $1\text{ k}\Omega$.

After starting the fracturing of the grain, new surfaces are generated in the intermetallic alloy, without the presence of oxides, facilitating hydrogen input, so that in the next 30 minutes we have a rapid drop in pressure and also in electrical resistance, while the electric capacity grows rapidly as the concentration of hydrogen increases in the alloy. During this time the volume of the grains increase, accompanying the increase of concentration. The grains, which were initially in an unstable situation, go now through a packing process, ending up by compressing each other locally, increasing the electric contact and contributing to the decreased resistance. With its dilated crystal lattice, there is a vertical movement of the grains, rapidly increasing the macroscopic volume of the powder bed, which is dramatically reflected in the increase of the electric capacity.

After this proof of concept, we envision the development of the method to exploit its full capabilities. The first obvious improvement is the use of an impedance spectrometer instead of measuring a single AC frequency. Resorting to more measuring parameters than those studied up to now in our system will give access to more physical parameters, like

those related to agglomeration effects that are evident in larger samples.

The method is also applicable to other materials, including insulating dielectric powders, for which it will be very interesting to study volume changes with absorption of hydrogen or any other gas.

3. Conclusions

One of the challenges in the usage of storage of hydrogen in solid materials as a vector for energy storage is related to the volumetric changes of a hydride that goes through hydrogen charging cycles. Various strategies are in use to avoid structural damage to the storage tanks due to stresses applied by the swelling powder bed on the walls and inner structures of the tanks.

Very recently, several independent groups identified the need to study in more detail the properties related to those volumetric changes, adding new techniques and equipment to their laboratory capabilities. Our group independently also identified the same challenge and, after completing the mounting and testing of the classical systems for the study of hydrides, designed and built a special system for that purpose.

The classical systems in use in our laboratory are a high-precision automatic Sieverts volumetric system, a low-cost volumetric system for automatic cycling through thousands of cycles, and an X-ray diffraction chamber for *in-situ* measurement of lattice parameters as a function of hydrogen content.

The new novel system is based on a coaxial capacitive sample chamber to be attached to the main volumetric system, allowing the measurement of the hydrogen content simultaneously with the AC electrical measurements done on the capacitive chamber. The electrical capacitance and resistance values obtained on these AC measurements are clearly and reproductively dependent on the volume occupied by a small amount of a hydride powder and its resistivity, the latter in a less sensitive manner. The physical parameters volume and resistivity are obtained from the primary capacitance and resistance values of the AC measurements by using a complex deconvolution algorithm that makes use of a carefully calibrated equivalent RC circuit of the chamber as a whole, including a specific equivalent circuit for the powder sample. The porosity of the powder is further obtained after considering the values of the lattice parameters, or the unit cell volume, of the hydride as a function of hydrogen content.

This proof of concept of the capacitive AC technique shows also the potential for further developments by adding more measurement parameters to the system. One immediate improvement is the use of impedance spectroscopy instead of single frequency AC measurements, as we have done so far.

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