

Perpectives and Challenges of Hydrogen Storage in Metal Hydrides. The Case of the CRES Wind-Hydrogen Plant

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In view of a future hydrogen-inclusive economy, there is a great need to develop safe, dense, and cost-effective methods to store hydrogen. Metal hydrides are formed by the reaction of hydrogen with metals, intermetallic compounds and their alloys. The reaction, also called absorption process is reversible, and therefore, it can be used to store hydrogen in a very restricted volume. A wide variety of materials has already been studied for the solid state storage of hydrogen, under various conditions of pressure, temperature and hydrogen density [1].

The main advantages of hydrogen storage in metal hydrides are a high volumetric density, the use of rather low pressures, and the possibility of long term storage without losses. On the other hand, the gravimetric hydrogen density is rather low and limited to less than 3% mass for hydrides operating at near ambient temperature and pressure. While a low gravimetric density is a drawback for transport applications, it is not essential for stationary applications.

If waste heat is available, the metal hydrides can play a dual role for both storing and compressing hydrogen. Hydrogen can be absorbed at low pressure and later recovered at a higher pressure, by supplying more heat than would be necessary for the desorption at a similar pressure. In such a case, the electrical energy needed to run a hydrogen compressor is spared either completely or to some extent, by avoiding the initial, energy-intensive compression stages.

One of the challenges for the development of solid state hydrogen storage is to better understand the interaction of hydrogen with metals, as well as the behavior of impurities present in the hydrogen flow. Metal hydrides can be used for the purification of hydrogen, since only the hydrogen molecule can enter inside the lattice, leaving the impurities in the gas phase or at the surface of the alloy.

At the wind-hydrogen plant of CRES in Keratea, Greece, the metal hydride tanks are based on the AB₅ family of intermetallic compounds, which generally crystallize into a hexagonal structure, and can absorb/desorb hydrogen at near ambient temperature. Hydrogen is produced by alkaline electrolysis at a maximum rate of 0.45 kg/h and at 2 MPa pressure. It is stored in six metal hydride tanks with a total capacity of 3.6 kg hydrogen. Hot water for the desorption of hydrogen is supplied by an electrical boiler (4 kW) and cooling water can be provided, if necessary, from a water chiller. Alternatively, hydrogen can be compressed up to 220 MPa in a single-stage compressor, to fill high pressure cylinders. All the components and utilities of the wind-hydrogen system are supplied by wind energy, but only the electrolyser can withstand power variations on a per second basis.

The metal hydride storage consists of 6 water-cooled sub-units, containing a metal alloy based on Lanthanum-Nickel (La_{1-x}Ce_xNi₅). It has been designed by the Frederick Institute of Technology, Cyprus, and manufactured by Labtech SA, Bulgaria. The mass specific hydrogen capacity is 1.28%w for the alloy and 0.66%w for the metal hydride tanks with cooling jackets. There is no pressure or temperature measurement inside the tanks, but the hydrogen pressure is measured on the line after the isolation valves, so it is equal to the pressure in the void space of the hydride tank when the valves are open. The water temperature is measured at the inlet and outlet of the cooling jacket, and therefore, the hydride temperature can be roughly estimated by extrapolation. The eventual presence of "hot spots" inside the tanks cannot be detected.

Hydrogen produced by alkaline water electrolysis generally contains small quantities of oxygen (0.2 to 0.5%v.) and is saturated with water vapour at the pressure and temperature of delivery. It may be purified by passing it through a catalytic deoxidizer, where the oxygen reacts with hydrogen producing more water vapour and a drier, in order to remove the humidity to the residual level desired. The reaction of oxygen and/or water with the intermetallic compound is strongly exothermic and, even if an explosion does not occur at such low concentrations, the hydrogen absorption capacity is expected to decrease. The effect of such impurities is not yet well understood.

In the present case, the oxygen content in hydrogen is approximately 0.2%v. and the humidity content corresponds to an atmospheric dew point of around 12°C. Three of the six hydride tanks are filled with the electrolytic hydrogen without purification, in order to study the effect on their cycling capability. Until now, the tanks have only been subject to a few dozens of absorption/desorption cycles, but the storage capacity has not decreased so far. An absorption experiment is shown in Figure 1.

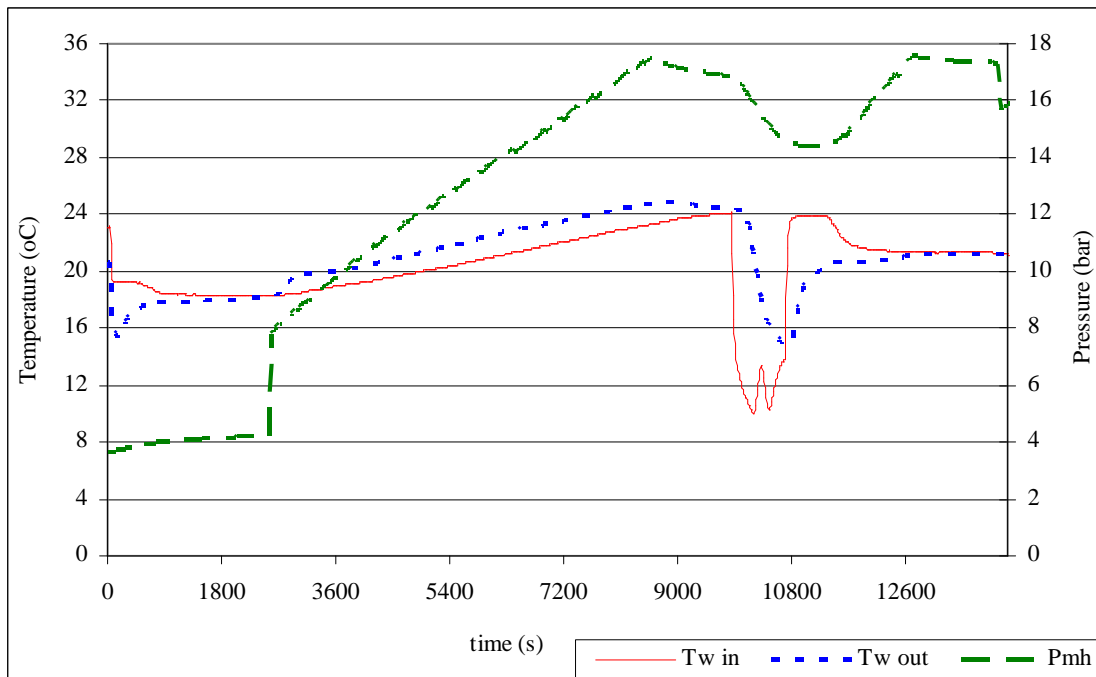


Figure 1. Hydrogen absorption in the metal hydride tanks.

In the experiment of Figure 1, the electrical boiler is not operating, but water from its reservoir is re-circulated in closed circuit, in order to absorb the heat from the hydriding reaction. Initially, the water temperature at the outlet of the cooling jacket is lower than at the inlet, because the temperature in the metal hydride tanks is lower than in the boiler reservoir. Once the water temperatures are stabilized (at around 18°C), the corresponding pressure (0.4 MPa), is considered as the initial equilibrium pressure. The main valve is opened and hydrogen is allowed in the metal hydride tank. The tank pressure increases instantly at the pressure of the hydrogen delivery line (0.8 MPa), because hydrogen fills the void space over the metal hydride. During absorption, the pressure increases gradually, and the heat produced by the reaction of hydride formation is used to heat up the water in the boiler reservoir. After approximately one and a half hours, the tank pressure approaches 1.8 MPa and the main valve is closed. Even without external hydrogen supply, the hydriding reaction continues, because the system is not yet at equilibrium. At some moment, cooling water from the water chiller is injected in the circuit for a few minutes and the system is allowed to reach an equilibrium. When the water temperatures are stabilized again (at around 21°C), the corresponding pressure (1.7 MPa) is considered as the final equilibrium pressure.

At the end of the experiment, the small decrease in pressure (down to 1.6 MPa) is due to a rapid venting (a few seconds) of the hydrogen present in the void space above the hydride tanks. This procedure was adopted, in order to vent the gas phase over the metal hydride, which may be enriched in accumulated impurities. The gas phase over the metal hydride cannot be continuously analysed, but the analysis of the oxygen in hydrogen content during the desorption phase has always shown values below 20-40 ppm. More investigations are necessary for a better estimation of the effect of the impurities on the performance of the hydrogen storage.

To the extent possible, the hydrogen absorption phase should occur without external cooling, in order to reduce the overall energy consumption of the system. In the same way, for the hydrogen desorption phase, it is also important to have a source of waste heat available, in order to avoid the use of an electrical boiler. Hydrogen storage in metal hydride tanks seems particularly interesting when it can be combined with a simultaneous purification and compression of hydrogen.