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Co-ordinator: Maximilian Fichtner, Karlsruhe Institute of Technology, Institute of Nanotechnology

Deliverable 5.5

WP Leader CNRS / M 48

Report on Lab-scale tank performance

Powder compaction and tank filling

About 400 g of NaAlH_4 infiltrated powder was provided by KIT. This pyrophoric material was packaged under protective atmosphere and introduced in glove-box immediately after reception.

Since the apparent density of this powder was rather low, it was planned to produce compacted disks by uni-axial compaction, using an embossing tool of 80 mm in diameter (figure 1). The matrix was filled in glove box, introduced in a plastic bag, then pressed in air. However, even after compaction the disk was not mechanically stable and the material burned in air, so that it was impossible to remove the disks. Then, we reduced the applied force from 1 t/cm^2 to 0.3 t/cm^2 to fabricate the disk within the glove box using a small press. But, the powder presents a very poor ability to compaction. A force of 0.3 t/cm^2 was not sufficient to induce a significant densification and the mechanical cohesion of these compacted disks was so weak that it appeared impossible to introduce them into the tank (figure 2).

Due to the difficulty to compact the material without further additives, the tank was filled with 4 successive batches of 50g of powder, which were compacted by hand directly in the tank. Metallic grids were installed to separate each batch. A central hole was drilled first into each grid in order to introduce 4 thermocouples into the material and to maintain them along the vertical axis (figure 3). Eventually, 200 g of powder were introduced into the tank. The charge was then reduced by half as compared to what was expected first (see Deliverable D5.1).



Figure 1: Embossing tool
($\varnothing = 80 \text{ mm}$)



Figure 2: early compacted disk removed
from the matrix

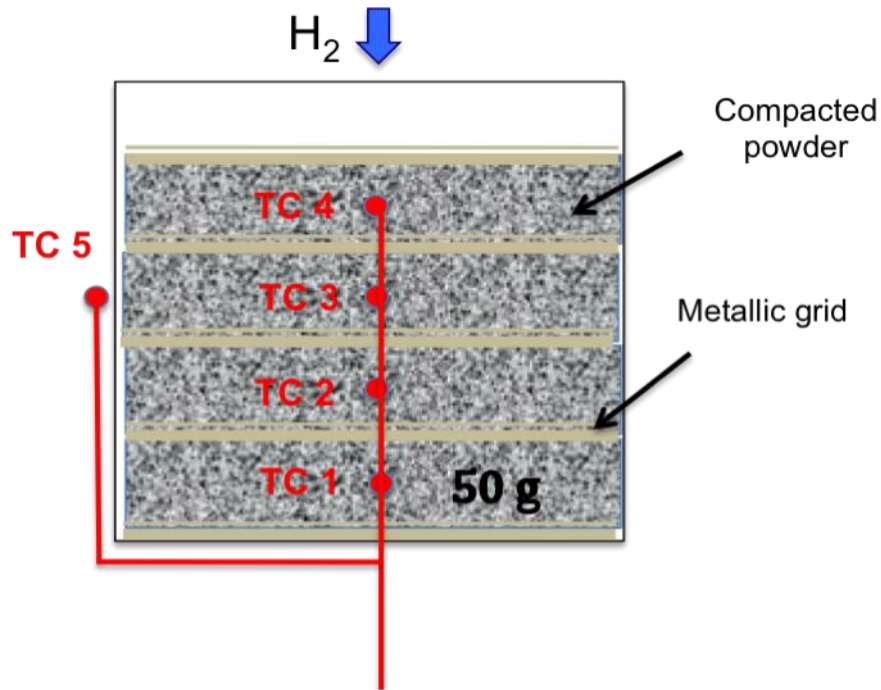


Figure 3: Location of the different thermocouples (TC1 to TC4 are located into the compacted powder ; TC5 is in contact with the external wall of the tank)

Gas volumes calculation

The tank was connected to the gas panel of the test rig, presented on figure 4. It includes mass-flow, safety valve, pneumatic manifolds and a water-cooled heat exchanger to cool down hydrogen gas before entering into the mass-flow. The total hydrogen volume absorbed or desorbed was integrated from the record of the mass-flow.

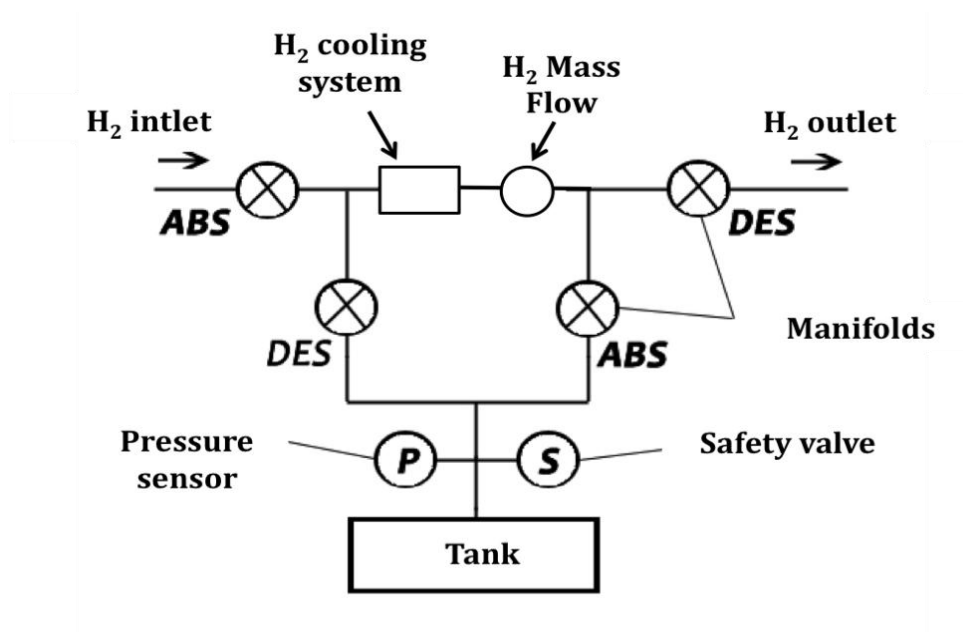


Figure 4 : Gas panel including pneumatic manifolds and heat exchanger to cool down H_2 gas.

To perform the absorption reaction a hydrogen pressure around or higher than 100 bars was applied. In that case the amount of hydrogen gas that is stored in the system is of the same order of magnitude than the amount of hydrogen absorbed by the material. This gas volume can be calculated from the recorded pressure and temperature, taking into account the “free” internal volume of the tank and the tube volumes on the panel gas. The free volume of the tank was calculated assuming a theoretical density of 1.25 for the infiltrated powder. The tube volume is mainly related to the contribution of the heat exchanger which is used to cool the desorbed gas before entering onto the mass-flow. These volumes are reported on table 1.

The real gas factor was used to determine the amount of hydrogen stored in the gaseous state. This volume was subtracted from the total volume recorded with the mass-flow to evaluate the hydrogen up-take absorbed or desorbed from the material.

Total internal volume of the tank	0.463 l
Material volume	0.16 l
Free internal volume of the tank	0.303 l
Tube volume for absorption	0.136 l
Tube volume for desorption	0.144 l

Table 1: Volumes accounted to calculate the amount of the hydrogen stored in gaseous state

Tank performance

The tank has been submitted to more than 20 hydrogenation cycles. During the first cycles, it was difficult to analyse the results since the manifolds fixed on the experiment were not sensitive enough to adjust the H₂-flow. Then the mass-flow tends to saturate during the beginning of the process and the recorded volumes were lower than expected. After 10 cycles, new manifolds were installed and the monitoring of the tank behaviour was reproducible.

1. Desorption tests

The outer temperature of the tank was monitored with a thermocouple in contact with the external wall (TC5 figure 3). Figure 5 shows a desorption process corresponding to the 13th cycle. The tank was heated up to 150°C under H₂ pressure. Then the H₂ pressure was progressively decreased from 130 bars to atmospheric pressure. Due to the mass-flow limitation (maximum 1 NL/min), it takes about 40 minutes to reach the atmospheric pressure. During this first period, the recorded H₂-flow was mainly due to the decrease of pressure. When the atmospheric pressure is reached, the hydrogen-flow decreases rapidly to 0.2 NL/min and becomes characteristic from the material itself.

The total H₂ volume and the H₂ desorbed from the hydride are reported on figure 6. The material desorbs mostly during the first 6 hours. However the hydride desorption continues until about 15 hours to deliver a desorbed volume of 45.6 NL. Taking into account the total amount of material into the tank (200g of NaAlH₄ infiltrated AC), it corresponds to a weight capacity of 2.0 wt.% (figure 9), which is in good agreement with the kinetics measurements performed earlier at KIT.

Due to the endothermic desorption reaction, a decrease of temperature is expected during the desorption process. The temperatures recorded into the tank are presented on figure 8. The thermal behaviour is very homogeneous, and only the thermocouple TC1 located close to the upper surface is a few degrees higher than others. Two steps are observed in the decrease of temperature. The first drop down corresponds to the reduction of pressure. It is

mainly attributed to the gas expansion. After pressure stabilisation, the temperatures continue to decrease at a lower rate, due to the hydrogen desorption reaction. When the reaction slows down, the temperatures increase progressively to the temperature set-point. The variations of temperatures remain less than 10°C, and the desorption rate is of the same order as for the kinetics early recorded on a small sample at KIT. As already predicted from numerical simulation, thermal exchanges have little influence on the tank discharging time.

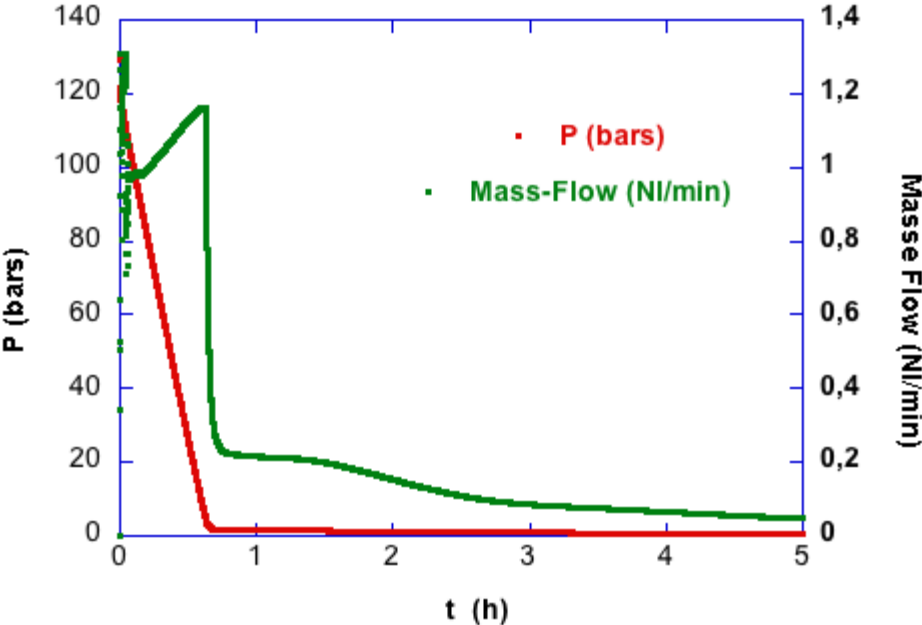


Figure 5: Hydrogen pressure and mass-flow recorded during a desorption process starting at 150°C and 130 bars (Cycle 13)

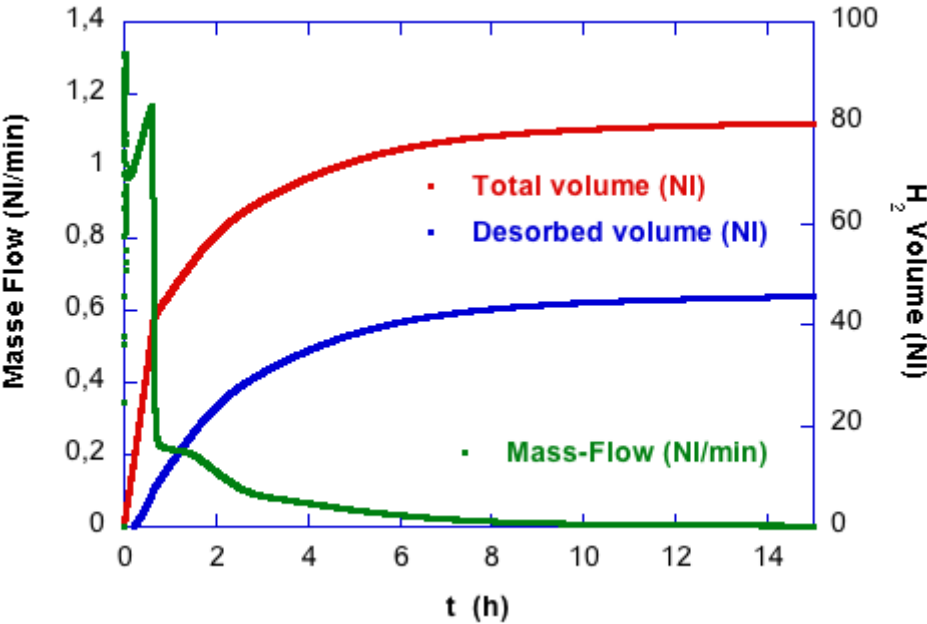


Figure 6: Total hydrogen volume recorded by the mass-flow during a desorption process starting at 135 bars and desorbed hydrogen volume deduced from the pressure variation

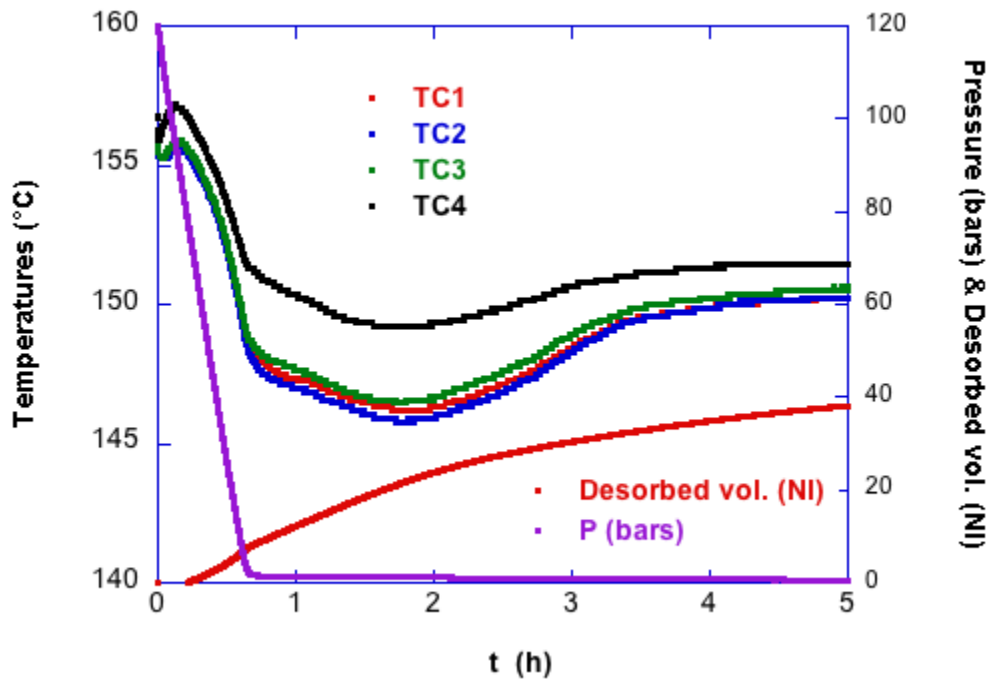


Figure 7: Pressure, desorbed hydrogen volume and temperatures recorded into the tank during the 13th desorption

2. Absorption tests

Absorption tests were performed starting at the same temperature of 125°C, and for different applied pressures ranging from 95 to 130 bars. Figure 8 shows that 24 hours are needed to complete the absorption of the uncatalysed material and that a pressure of 95 bars is not enough to achieve a fully hydrogenated state. Again, the increase of temperature is limited to about 10°C. Thermal exchange has little influence on the tank loading time due to the moderate kinetics of reaction and relative high thermal conductivity of the infiltrated materials.

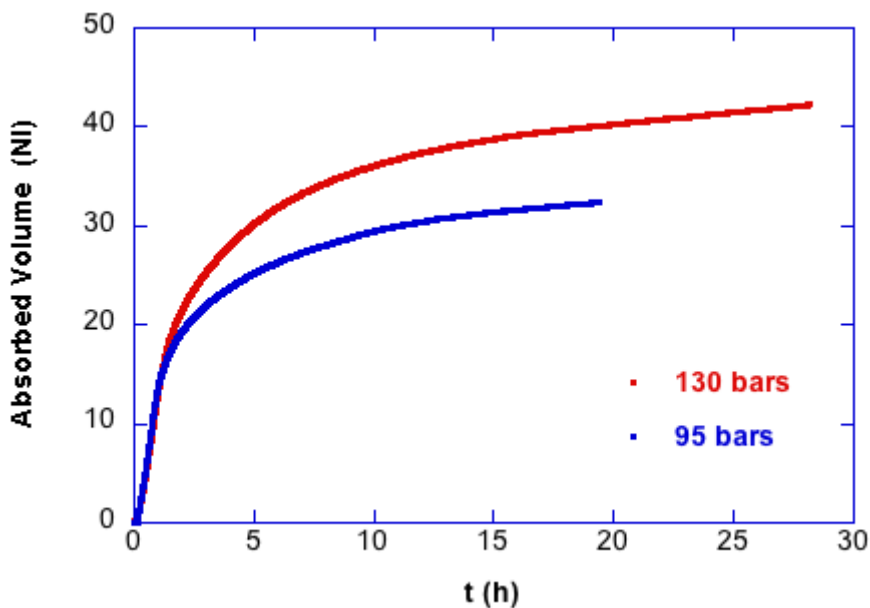


Figure 8: Absorbed hydrogen volume recorded for 2 different applied pressures

Cyclability

In figure 9 are reported 4 successive desorption tests performed under the same experimental conditions. A very good reproducibility of the tank behaviour is observed and the material appears very stable upon cycling. The hydrogen mass is referred to the total amount of composite material in the tank (200 g). However, if the amount of NaAlH_4 only is taken into account, the maximum corresponds to a desorbed gravimetric capacity of 3.5 wt.%. This value is very close to the theoretical value of 3.7 wt.% expected for the first step of the reaction ($\text{NaAlH}_4 \Leftrightarrow 1/3 \text{Na}_3\text{AlH}_6 + 2/3 \text{Al} + \text{H}_2$). It confirms the good cyclability of this material.

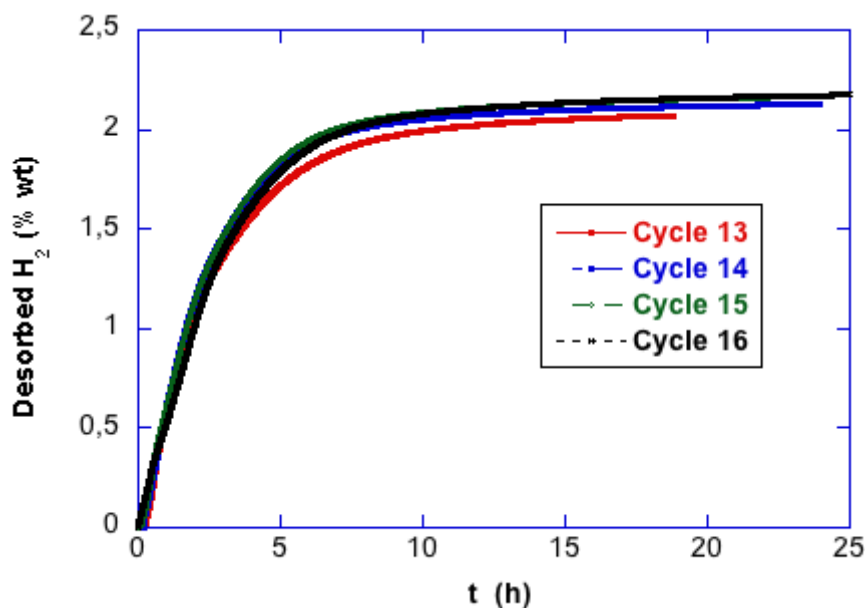


Figure 9: Hydrogen mass desorbed from the material at 150°C (cycles 13 to 16)

Coupling with fuel cell

As demonstration, the tank was connected to a small Fuel Cell developed by PaxiTech. The tank was able to supply the Fuel Cell for more than 48 hours.

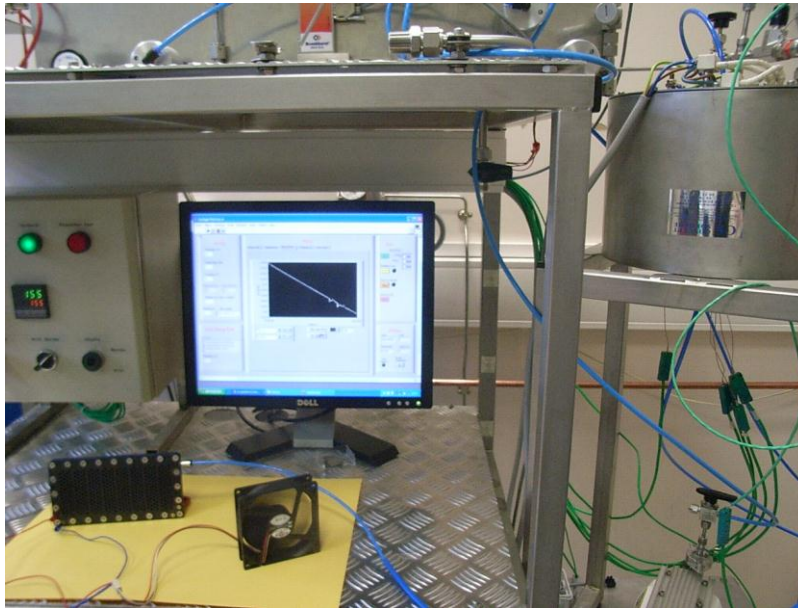


Figure 10: View of a small PEMFC supply with the tank

Conclusion

- NaAlH_4 infiltrated powders are pyrophoric and exhibit a poor ability for compaction in pure form, without additives. In these first attempts it was almost impossible to produce compacted disks and the material volumetric density was limited to about 11 g of hydrogen per litre.
- The amount of hydrogen stored in gaseous state was of the same order of magnitude than in the material, so that the resulting volumetric density was of about 18 g per litre.
- The thermal conductivity of the infiltrated material is about 10 times larger than that of pure NaAlH_4 powders. Hence, the thermal behaviour of the tank is very homogeneous and thermal exchanges have little influence on the loading time. Nevertheless, for an industrial size tank, careful attention should be paid to check that the increase in size does not invalidate this conclusion, especially if reaction kinetics are improved.
- The tank was submitted to more than 20 hydrogenation/dehydrogenation cycles. A very good cyclability has been shown, with a material gravimetric capacity very close to the expected value corresponding to the first step of the reaction ($\text{NaAlH}_4 \Leftrightarrow 1/3 \text{Na}_3\text{AlH}_6 + 2/3 \text{Al} + \text{H}_2$).
- The system gravimetric capacity was low because the laboratory tank was designed to withstand a pressure of 200 bars and the internal volume for the hydride was comparably small compared to the flanges etc. In order to reach a reasonable gravimetric capacity, stainless steel should be replaced by another material and the amount/volume of active material should be increased.