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Design, sorption behaviour and energy management in a sodium alanate-based lightweight hydrogen storage tank

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Abstract

A lightweight tank for hydrogen storage based on four kilograms of sodium alanate was designed, built and tested. An improvement in gravimetric capacity of 83 % and 49 % in volumetric capacity over a previous tank was achieved. Heat evolution and temperature spikes during hydrogen absorption were studied. Due to the high specific heat of the complex hydride, the storage material itself acts as a heat sink, aiding in the heat management of the system. The first-ever radiography with fast neutrons on an operational complex-hydride based test tank was performed.

Keywords: sodium alanate, hydrogen storage, scale-up, tank design, heat management

1. Introduction

Hydrogen storage in complex hydrides, notably doped sodium alanate, has been studied since 1996. There is a lot of information on this system, which can hardly be cited to completion, but it concerns mostly a laboratory scale and expanded graphite, milled in five batches of >1.4 kg each, as previously published and used in the previous tank from project STORHY. The only difference is that the amount of Al was in excess of the stoichiometric one: 1.09 to 1. This has shown to be beneficial to the hydrogen storage capacity. The amount of storage material was 4413.4 g. The material for the tank hull, since it needed to be as light as possible, was a Ti Grade 2 alloy (3.7035), which is used in the chemical industry because of its high corrosion resistance. In our case it is possible to use it because the Ti in this alloy is almost exclusively α phase, which has a limited diffusivity for hydrogen in the crystal structure, therefore hindering the process of hydrogen embrittlement. However, our calculations show that the usage of duplex steels with a tensile strength of 267 MPa at 200 °C and the optimization of the shape by eliminating the front flange would increase the system’s gravimetric capacity from 1.7 wt % (@ 4.5 wt % material capacity) to 2.3 wt %. Unfortunately, these specialized steels could not be obtained at the time of the project in the desired geometry. For future tanks, these options will be pursued, since it not only offers an improved gravimetric capacity, but also easier and more cost-effective fabrication due to the difficulties of Ti welding. Reduced prices in comparison with titanium when entering se-
ries production are also an important consideration. The present tank, developed during the European project NESSHY, is a tube-and-shell system consisting of an internal cylindrical hull of 80 mm inner diameter with a hemispherical cap at one end and a flange at the other (Fig. 1), as well as an outer cylindrical hull with welded torispherical and flange ends. The internal hull weighs 8.4 kg and has an internal volume of 4.9 liter. Wall thickness is 5 mm. The flange end was used to load the storage material, compressed to annular pellets 77 mm in outer diameter and ~15 mm thick (Fig. 2). The difference of 3 mm to the inner diameter of the tank was included to allow for pellet expansion during cycling. Pellets have several advantages that contribute to make the tank lighter, as desired: their porosity is lower than that of loose powder, so that more storage material fits into the same volume. This increases volumetric capacity, in this case to 31.2 kgH$_2$/m$^3$, but also gravimetric capacity, since the volume is bound by the tank hull, which has a constant weight. The sum of hull and storage material weight is higher, but the amount of hydrogen stored also increases, thus increasing the hydrogen to system weight ratio. This is especially important for lightweight hydrides like sodium alanate, since the weight of the hull contributes greatly to the overall system weight.

Another advantage of pellets is that they have a better heat transfer behaviour, since there is less empty space between the powder grains. Heat conduction in the solid state is therefore improved, leading to better kinetics and, under the right circumstances, higher gravimetric capacity.

The tank was instrumented with temperature sensors both within the inner titanium hull (in order to measure the temperature in the hydrogen storage space) and in the space between the inner and the outer hulls, where a heat exchange fluid was pumped through in order to bring the tank to the desired temperature. As part of the tank test rig described elsewhere, a Coriolis sensor measured the heat transfer fluid flow and temperature sensors at the inlet and outlet of the heat exchange space allowed the measurement of the temperature drop or increase in the heat exchange fluid.

The tank was analyzed after cycling for 33 times via neutron radiography at the FRM II facility in Garching, Germany. The NECTAR beamline was used due to its operation with fission (fast) neutrons in the energy range around 1.8 MeV. These high-energy neutrons are capable of penetrating thick material samples and are thus ideal to image the NESSHY tank. The conditions used for the imaging are: measuring time: 60 sec.; 60 dark images, 10 open beam images, one image of the tank each at 420, 320, 120, -120 and -270 mm from center. Additionally, two images of the top of the tank were taken. All images were filtered, dark image corrected and normalized before being put together manually.

3. Results and Discussion

The hydrogen sorption behaviour of the lightweight tank (Fig. 3) was similar to that observed in the previous model, albeit slightly slower, since the greater diameter of the hydride bed made it more difficult for the heat to be dissipated during the hydrogen absorption. The experimentally determined total capacity (ratio of material + gas phase hydrogen mass to hydride mass) is slightly lower at around 4 wt% instead of 4.5 wt%. The reason for this is still unclear, although it may lie in the fact that the hydride bakes together into a solid lump, therefore creating zones in the tank that cannot be reached by the gas dur-
ing hydrogenation. However, the difference between the total and the material capacity has been reduced from 0.6 to 0.13 wt%, meaning that the free volume not being used by storage material has been substantially reduced. For this reason, the system capacity reached was 1.58 wt% instead of the aimed-at 1.7 wt%. The desorption (Fig. 4) shows that a steady flow of hydrogen (in this case, 3.7 normal liters per minute) can be maintained for an extended period of time, while the material supplies enough hydrogen to keep a quasi-constant pressure. Normalizing over the sample amount in this tank (4.4 kg of alanate), the possible flow for a scaled-up tank can be calculated for a full-size, automotive-style tank for 4 kg of hydrogen. In this case, a constant flow of 9.6 g · min⁻¹ could be maintained using these conditions (170 °C and starting pressure of 100 bar) for around 92 minutes (the time of constant pressure after the operational temperature has been reached). It can be certainly more than doubled if the pressure inside the tank is of no consequence and in a modular tank by only heating the modules that are releasing hydrogen and not using those that are still full or heating the ones that are already empty.

An issue that is extremely important for solid state hydrogen storage is that of heat management, both for de- and hydrogenation. For hydrogenation, the reaction heat needs to be removed at a fast pace in order to charge the tank in the amount of time allocated depending on the application. For dehydrogenation, the reaction heat needs to be supplied in a timely fashion in order to maintain the flow of hydrogen at the desired level. In both cases, thermal inertia is to be expected in scaled-up systems where large amounts of hydride need to change temperature, either for startup or switching from charging to discharging modes (or vice versa).

In the present case, the amount of heat evolved by the tank during hydrogenation and dissipated over the heat exchange fluid was calculated by using the temperature difference in the heat exchange fluid between the inlet and the outlet of the tank, its mass flow and its heat capacity (Marlotherm® X, 2.05 kJ · (kg · K)⁻¹ at 120 °C). It can be seen (Fig. 5) that the heat flow closely resembles the two-stage chemical reaction, with one high peak for the formation of the Na₃AlH₆ (2.07 kW at the maximum) and a shoulder starting below 0.55 kW for the slower formation of NaAlH₄. Total heat emission was 2326 kJ. The hydrogen flow was restricted to 245 lₙ·min⁻¹, thus the time of around 120 minutes for the two reactions (albeit not to 100 % completion, as seen in Fig. 3) instead of around 17 minutes (less than 10 minutes for 80 % capacity) as in the previous tank running at a maximum of 2500 lₙ·min⁻¹. This extended reaction time is partly responsible for the low peak heat flow detected. When scaling up to a 4 kg H₂ storage tank, the corresponding peak heat flow would be a mere 49 kW.

It is thus the wish for rapid charging of hydrogen storage tanks that make the cooling requirements high or low. For applications where a (relatively) slow charging of the tank is permissible, solid-state storage is an interesting alternative to conventional storage due to its low pressure operation, binding of the hydrogen in a chemical form (which avoids the danger of ex-
plosive discharge present in high-pressure tanks) and thermal integration with the host systems for more efficient usage of available heat. The other reason for the low peak in heat flow is the fact that the storage material has a high specific heat capacity

\[ \text{heat capacity} = \frac{1.5 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}}{\text{for NaAlH}_4} \quad \text{and} \quad \frac{1.47 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}}{\text{for Na}_3\text{AlH}_6} \]

at 298.15 K, as compared to iron: \( \frac{0.449 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}}{\text{for NaAlH}_4} \).

The neutron imaging at the NECTAR beamline yielded an image (radiograph) of the inner side of the tank (Fig. 6).

In this image, the dark zone in the middle and right-hand side of the tank shows the sodium alanate pellets inside the tank. Remarkably, most of the material seems to have kept its shape and position despite the road transportation from Geesthacht to Garching (more than 700 km). At the fore end of the tank, a pellet seems to have fallen away from the others and to be lying on its side. There is also a shadow at the head of the reactor (but behind the flange) covering the lower half of the tank. This may be sodium alanate powder that has been mechanically taken out of the pellets, either during cycling or during transportation and has been deposited over the lower half of the cylinder. Due to its lighter colour, it is probably just a thin layer and not a filling of powder, but only after opening the tank or by neutron tomography it can be ascertained for sure. Moreover, it is clear from this picture that the empty space left at the front of the tank in order for the pellets to expand has not been used. The pellets expanded radially, but not axially, or at least not as much as other authors measured when using unconstrained pellets.

4. Conclusions

A tank was designed and built that managed to improve on the weight and volume of its predecessor by a considerable margin. While the kinetics of absorption were not demonstrated to be as fast as that measured in the previous model, the design has the potential to equal, if not surpass it in this aspect as well. Especially the use of pellets instead of loose powder, which contributes considerably to the improvement in volumetric capacity, is also a key to both an improvement in heat transfer characteristics and tank stability and usability, as shown in the neutron radiography performed at the FRM II in Garching.

The heat transfer behavior was studied closely for this tank, showing that the peak heat emission during hydrogenation was relatively low even when using low heat transfer fluid flows (25 kg/min, 16 % of full flow). This is due not only to the longer hydrogenation times, but also to a mechanism not previously considered in lab scale experiments: the self-heating of the storage material. The high heat capacity exhibited by the solid reactants and products means that a considerable proportion of the heat produced during the hydrogenation reaction is already consumed in the process of increasing the temperature of the storage material. In a hydrogenation, around 2300 kJ (0.64 kWh) of energy were dissipated to store 173 g of H\(_2\); that is 9.4 % of the energy content of 24541 kJ (or 6.82 kWh) in the hydrogen. Since this can be eliminated (or even used) via conventional heat exchangers, the system compares favourably with other techniques which have similar or higher requirements for energy dissipation and do so at low or cryogenic temperatures, increasing the complexity and cost of such alternatives.

In sum, we have shown that the lightweight sodium alanate system can be, with some improvements, a
viable hydrogen storage alternative for certain scenarios, especially in the area of stationary, large scale hydrogen storage.

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References


