Innovative Hydrogen Storage Solutions for Aerospace Applications

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Innovative hydrogen storage solutions are increasingly important for a number of future aerospace applications [1]. The Austrian Institute of Technology (AIT) is presently developing an innovative hydrogen storage system based on a combination of high pressure storage in hollow microspheres and chemical hydrogen storage. Our patent-registered system provides a double hydrogen generation process without any external energy or heat during storage or gas release. Analysis shows that such a system can reach hydrogen storage capacities of up to 10 wt% at ambient pressures and temperatures in theory. Gaseous hydrogen was stored in hollow glass microspheres (5 – 200 µm diameters) under high pressure (140 – 700 bar). The sphere-wall is impermeable for hydrogen at ambient temperature; the heating of the spheres increases the diffusion of hydrogen through the wall. Disadvantages of this storage method are the required high heat quantity of the microsphere due to the low thermal conductivity of glass ((0.1 – 0.2 W/(m*K)). The innovative AIT system consists of three stepps [2]. In the first step, water is used as a functional liquid to carry the hollow glass microspheres which are loaded with up to 700 bar of hydrogen gas. NaBH4 were injected together with the glass microspheres into a reaction chamber. There the water reacts catalytically with the $NaBH_4$ producing hydrogen, $NaBO_2$ and heat. This heat was used to release the hydrogen from the hollow glass microspheres. The spheres are coated with a catalyst. Hence most of the $NaBH_4$ is converted at the surface of the spheres due to the catalyst. The heat production has a maximum value at the surface of the spheres which increase the overall efficiency. All end products in this process (empty microspheres and sodium metaborate) are recyclable and can be filled again respectively. The storage capacity depends on the sphere dimensions and the weight of the spheres, the hydrogen pressure and the used hydride. First microsphere filling tests were done during 2 weeks in a high pressure autoclave at 250 °C and 700 bar maximum pressure. Further hydrogen filling tests were done during 1 week at 150 °C and 140 bar. The permeation of hydrogen through the wall depends on the hydrogen diffusivity. It is a function of the temperature, the composition of the sphere material, the wall thickness, the pressure difference and the exchange area. Some previous made heating tests with filled S38 microspheres (350 bar and 700 bar) from 3M™ at different temperatures showed that the released hydrogen was nearly the same due to the fact that the 700 bar microspheres had an age of 100 days and hence approx. half of them were broken during this period. This can be explained with the fact that the S38 spheres have a minimum fractional survival of 80 % at 280 bar. Storage capacities of about 1.9 wt% were achieved at 190 ° after 19 hours. Recent tests with S38 microspheres (filled with 140 bar hydrogen) showed no diffusion process at RT and no broken spheres. This confirmed the assumption, that long-time gas storage in microspheres is possible, if the pressure of the minimum fractional survival rate is higher than the filling pressure. Hence high pressure gas storage up to 700 bar seemed to be possible for example with S60hs or iM30K microspheres. Another important part of the storage system was the coating of microspheres with different catalysts. We coated the microspheres with two different catalysts based on rhodium and platinum and two different methods – a wet chemical sol gel process and a sputtering process. The different coating technologies results in different coating properties. The sol-gel coated microspheres have no consistent coating layer in contrast to the sputtered microspheres. Furthermore some spheres were backed or were broken during the process. Only a couple of spheres were broken during the sputtering process. Sputtering seemed to be an applicable process for microsphere coating. The sol-gel method is not suitable due to the fact that the coating is not firmly connected with the microspheres and could be washed down from the spheres. The sputtered microspheres showed good reaction rates in combination with sodium borohydride injection. During the tests an uncommon thermal behavior was observed. The temperature inside the chamber reaches it maximum after a few seconds without microspheres at a heating test. Uncoated microspheres reach its maximum temperature after a few minutes due to their very low thermal conductivity. The maximum temperature is 35% lower due to the additional mass of microspheres. The coated spheres should show the same behavior, but the maximum temperature is only 40% of the uncoated microspheres. Furthermore the temperature reaches its maximum after a few seconds. Both results can be explained with a significantly higher thermal conductivity of coated microspheres versus uncoated microspheres, in spite of the very low coating layer thickness of about 4 nm. The experiments were done with platinum sputtered microspheres, whereas the thermal conductivity of copper is more than 5 times higher for example. Further tests have to be done to verify our results. This includes tests with higher pressure (350 bar and 700 bar) and long-time gas release tests. Furthermore additional tests will be done with helium instead of hydrogen to demonstrate the possible use of microspheres as innovative helium storage system. The diffusion mechanisms and the diffusivity of helium and hydrogen are similar but at different temperatures. The required lower temperatures for helium could be realized via an electrical heating unit, if the thermal conductivity of microspheres could be increased significantly by sputtering. Applications for hydrogen filled microspheres were identified in the area of hydrogen generation on satellites, additives for cryogenic fuels, radiation safety and biogas upgrading. Helium filled microspheres could be used to replace high pressure tanks on telecom satellites. The figure shows uncoated (left) and copper sputtered microspheres (right).

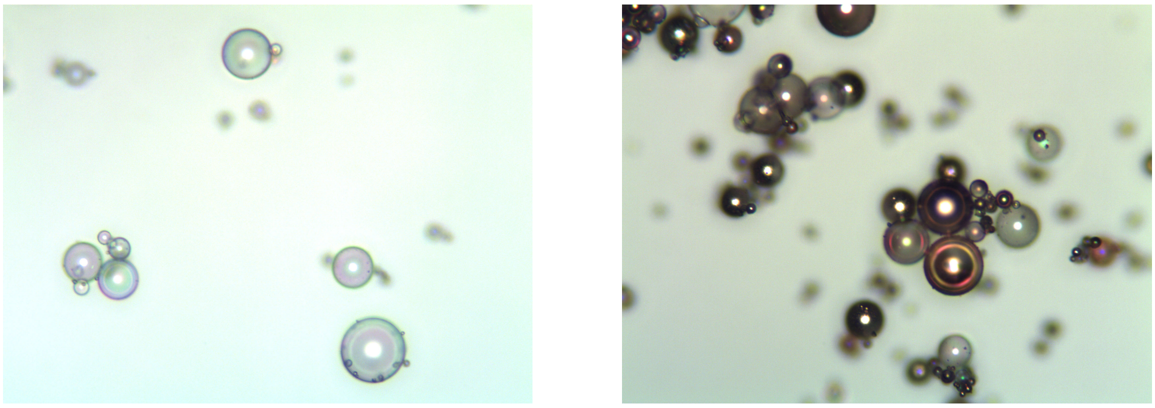

Figure 1: Picture of uncoated (left) and copper coated (right) microspheres.

Another project deals with new energy storage solutions to replace APU's or secondary batteries on satellites or aircrafts [3]. We decided to approach this topic by combining a fuel cell with innovative chemical hydrogen and oxygen storage as well as integrating the oxygen storage system into a form that can be used as a structural element. This advantage would be very interesting in order to obtain higher weight efficiencies. Another advantage is the direct integration of the fuel cell into the hydrogen storage material. Thus the power dissipation of the fuel cell can be used for desorption of hydrogen where heat is required, instead of being rejected by a heavy thermal control system. In this project, gaseous hydrogen was stored in a metal hydride (MH). Sodium alanate seemed to be particularly suitable for reversible hydrogen storage on satellites due to its high storage capacities at relatively moderate temperatures and pressures as well as the fact that it is commercially available and lots of kinetic measurement data is available. Sodium alanate is a crystalline complex hydride with tetragonal form. It is colourless and highly sensitive against hydrolysis. It reacts in a three step dehydrogenation reaction and can release 7.4 wt% of hydrogen. The first step is the conversion of $NaAlH_4$ to Na_3AlH_6 under aluminium and hydrogen separation. The second step is the conversion of Na_3AlH_6 to NaH under aluminium and again hydrogen separation, and the third step is the conversion of NaH to Na under hydrogen separation. However NaH is a highly stable composition and requires high temperatures for separation (approximately 400 °C) which is not acceptable for technical use. A limitation of the process to the first two steps decreases the hydrogen capacity to 5.55 wt%, but also reduces the desorption temperature to less than 150 °C. In order to derive an optimal tank structure, as well as predict the thermal characteristics of any future MH system design, the physical processes during the hydrogen storage and release have been implemented into a coupled fluid/thermal finite elements model using ANSYS™ integrated programming language APDL. A well established model has been applied for the reaction kinetics of absorption and desorption processes of hydrogen containing the four physical processes of chemical sorption, surface transition, diffusion and phase transition. Each of these processes runs at a rate determined by time-dependent parameters. The overall absorption speed of H_2 is determined by the minimum taken over the four processes listed above. For desorption, the process is limited by the maximum. Hence it is necessary to simulate all four processes, and calculate the extremal values at each time step. In addition thermal conduction and forced convection by a cooling fluid were taken into account. With a first demonstrator prototype, ca. 500 litre H_2 could be stored into 1 kg of sodium alanate which represents a gravimetric density of more than 4 % [4]. The temperature distribution corresponds to the results of the simulation, which verifies the simulation as well as the reactor (so called cheese-) concept forming very homogenous temperatures within the tank. Finally all these test results triggered our interest in developing a hydrogen storage tank based on metal hydrides to replace high pressure tanks in regenerative fuel cell systems (RFCS). The biggest advantage in comparison with high pressure tanks is the possible use of metal hydrides as heat storage system as shown in Figure 2. The main advantage of using a MH in the RFCS is that the power dissipation of the FC (>60% of the generated electrical power, depending on the RFC efficiency) can be used for desorption of Hydrogen where heat is required, instead of being rejected by a heavy thermal control system. The heat is stored in the MH and can be rejected during the loading cycle. Thus, thermal peak loads, for example during energy provision on a telecom satellite, can be avoided completely.

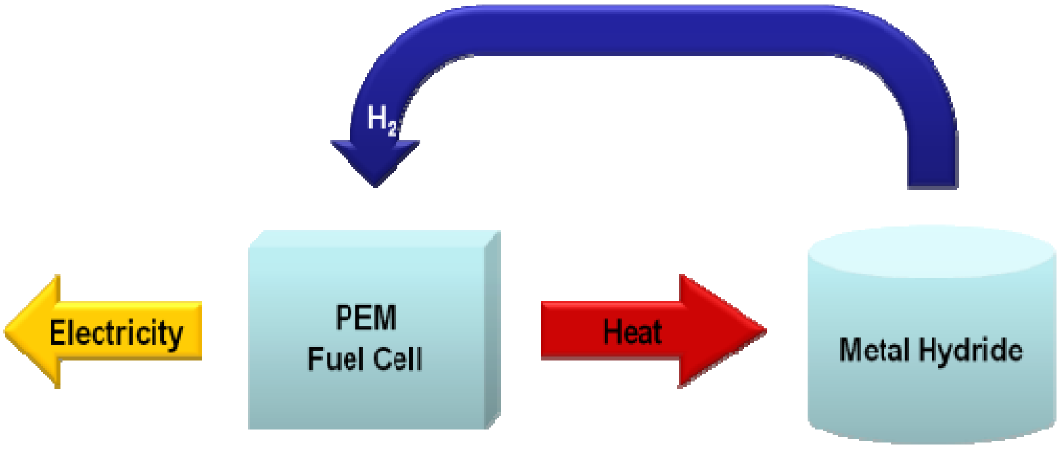

Figure 2: Heat storage during energy provision.

Terrestrial fuel cells take the oxygen from ambient atmosphere; hence they do not require oxygen storage tanks. Space applications require oxygen storage, which is usually realized with pressurized gas tanks or solid gas generators. The reversibility of both solutions is difficult, e.g. the compression of gas into a tank requires a large and heavy compressor. We are currently developing a novel reversible oxygen storage solution based on $YBaCo_4O_7$ [5]. The temperature of oxygen as well as $YBaCo_4O_7$ must be at least 350 °C for the absorption of oxygen. Furthermore the medium should be completely surrounded by an oxygen atmosphere. The absorption/desorption behaviour has been measured with a special thermo gravimetric analysis. Such analysis determines changes in weight in relation to change in temperature. The expected rise of weight for the compound is approximately 3 wt%, which equals the absorbed mass of oxygen. The achieved storage effect for the first tests was approx. 35 % of the maximum storage capacity. This could be explained by different particle size distribution, a non-uniform air flow through the material and different pressures inside the reactor. Further tests have to be done to optimize the material and the measurement system. Based on these results, we will simulate and design the overall reversible oxygen tank system.

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