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Detlef Stolten, Thomas Grube (Eds.):
18th World Hydrogen Energy Conference 2010 - WHEC 2010
Parallel Sessions Book 4: Storage Systems / Policy Perspectives, Initiatives and Co-operations
Proceedings of the WHEC, May 16.-21. 2010, Essen
Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-4
Institute of Energy Research - Fuel Cells (IEF-3)
Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010
ISBN: 978-3-89336-654-5

HT-PEM Fuel Cell System with Integrated Complex Hydride Storage Tank

R. Urbanczyk, **D. Bathen**, Institut für Energie- und Umwelttechnik e.V., Germany
M. Felderhoff, Max-Planck-Institut für Kohlenforschung, Germany
J. Burfeind, Zentrum für Brennstoffzellentechnik GmbH, Germany

1 Introduction

The growing gap between demands for economic growth and better standard of life on one hand and care for global climate and decreasing energy resources on the other hand require sustainable solutions in the near future. One answer to these problems might be the increased use of renewable energies and "clean" energy carriers like hydrogen wherever possible. Among other things, hydrogen storage is one of the major challenges encumbering hydrogen economy. There are three common techniques of hydrogen storage:

- Pressurized hydrogen
- Liquefied hydrogen
- Hydrogen reversibly chemisorbed or physisorbed (metal hydrides, MOF, carbon materials)

However, the energy required to store hydrogen in each storage method is quite different. For instance, the necessary cooling energy for liquefied hydrogen amounts to 30 % of the stored chemical energy of hydrogen in relation to its lower heating value. An energy input of 12 % for pressurizing hydrogen up to 200 bar [1] and 9 % for storing it at 100 bar in a metal hydride (e.g. $NaAlH_4$) will be required.

A fuel cell system described here was developed and tested with a hydrogen storage tank based on the metal hydride sodium alanate which was thermally coupled to a high temperature fuel cell (HT-PEM). The fuel cell was fed by hydrogen desorbed from the storage tank while the fuel cell provided the reactor with the necessary heat for desorbing hydrogen. The project was carried out by following institutions: Zentrum für BrennstoffzellenTechnik (ZBT) in Duisburg, Max-Planck-Institut für Kohlenforschung in Mülheim (Ruhr) and Institut für Energie und Umwelttechnik (IUTA) in Duisburg. ZBT has developed the HT-PEM fuel cell stack (Figure 1), MPI produced the metal hydride sodium alanate material and IUTA constructed and tested the hydrogen storage tank.

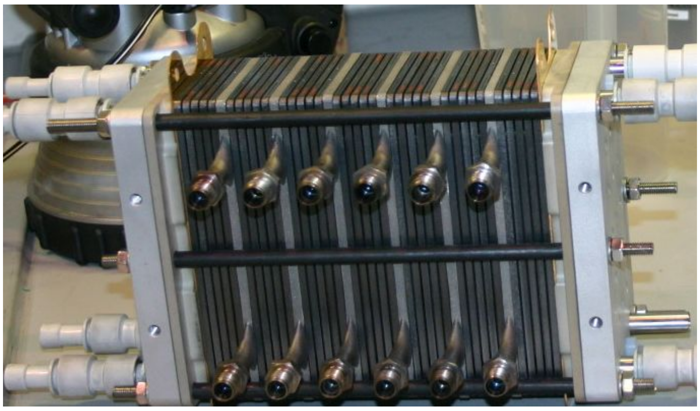

Figure 1: Liquid cooled HT-PEM-Stack with 28 cells by ZBT.

2 Experimental

For gaining experience in constructing and operating hydrogen storage tanks based on sodium alanate the reactor was developed in three steps. The first tank had an inner volume of 245 ml and 67 g of hydride material charged inside. The material was doped with 4 mol-% of $TiCl_3$ and the hydrogen capacity reached 3.35 wt.-% (theoretical reversible storage capacity is about 5.5 wt.-% [2]). The hydrogen mass adsorbed in the hydride was 2.2 g. The heating of the tank was performed by thermal oil flowing in two 1/8 " u-bends welded at the lid. Contrary to the first prototype, the second tank was designed with two flanges. This facilitated the charging of the reactor with the metal hydride and made the changing of the heating systems inside the tank for test purposes more flexible. The first version of the second prototype included a spring-plate system connected to the lid in order to compensate for the volume change of metal hydride during the operation [3]. The heat transfer in this tank was realized by thermal oil flow in annulus. The fluid was led in helically wound rectangular channels inside for heat transfer improvement. The 2^{nd} reactor was charged with 241 g of sodium alanate at 4 mol-% of $TiCl_3$, which resulted in 8 g of hydrogen evolved in the first cycle. This relates to 3,35 wt.-% of hydrogen content in the material. The tank was operated both in stand alone mode and coupled with the HT-PEM as well. In the stand alone operation the absorbing and desorbing characteristics were investigated. In each case the system was heated up and at the end of the test cooled down by a thermostat. The hydrogen flow was adjusted by a mass flow controller. The cumulated hydrogen mass was then calculated by the measurement software. The absorbed hydrogen mass was estimated either volumetrically or with mass flow meter. The mass flow of the cooling medium was measured by a coriolis mass flow meter. The sketch of the test rig is shown in Figure 2.

It was necessary to heat up the system at the beginning of the test. The oil flew first through the heat exchanger system in the tank and then in the channels of the fuel cell. After both components reached appropriate temperature levels, the pump of the thermostat was switched off and the oil flow was driven by the second pump (in Figure 2 between tank and fuel cell).

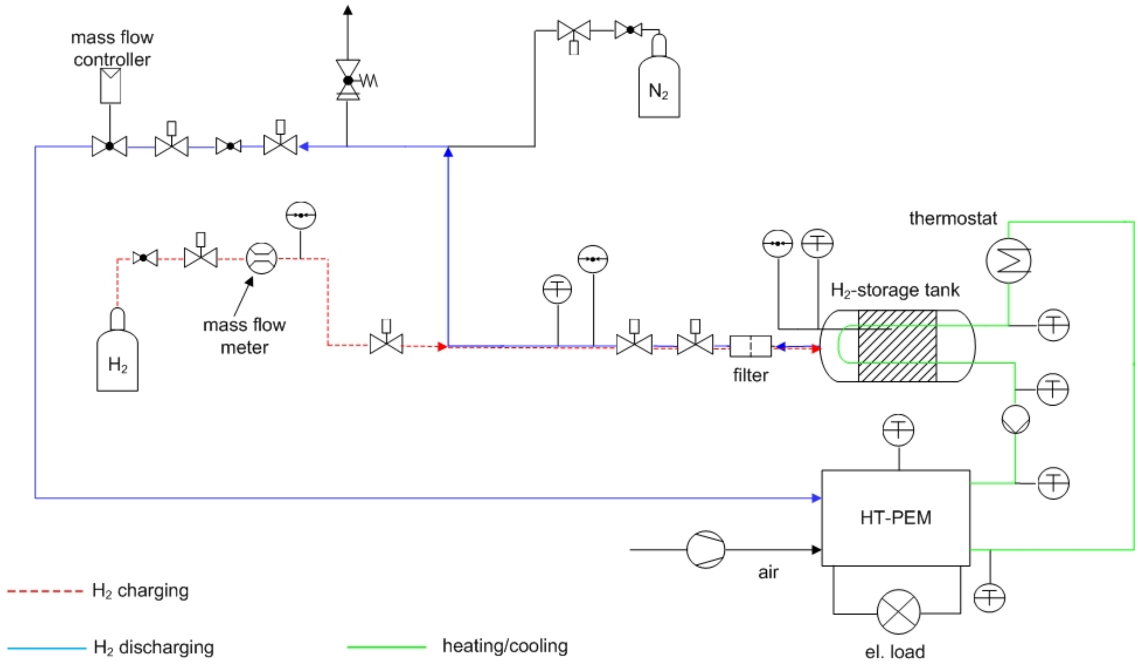

Figure 2: **Sketch of the test rig.**

The experiments carried out with the above mentioned two reactors led into construction and subsequent tests with the scaled up version of the tank depicted in Figure 3. The vessel contained 2676 g of sodium alanate doped with 4 mol-% of $TiCl_3$. The inner volume of the tank amounted to 5.1 l and 7 thermocouples were installed for temperature measurements. The heat transfer was realized by a system of a double coiled helical winding inside the tank and additionally in the annulus. In the last one the oil flow was led by a rectangular coil with 8 turns. The inner and outer coil inside of the reactor was made of 15 turns of 6 mm outer diameter pipe. The pressure vessel was machined from austenitic steel X 6 CrNiMoTi 17-12 2.

In this project ZBT developed a HT-PEM fuel cell stack with 28 cells with an output power of 260 W_{el}. The operating temperature range of the stack was 120-190°C. The heat transfer in the fuel cell was realized by oil flow inside of 6 cooling plates.

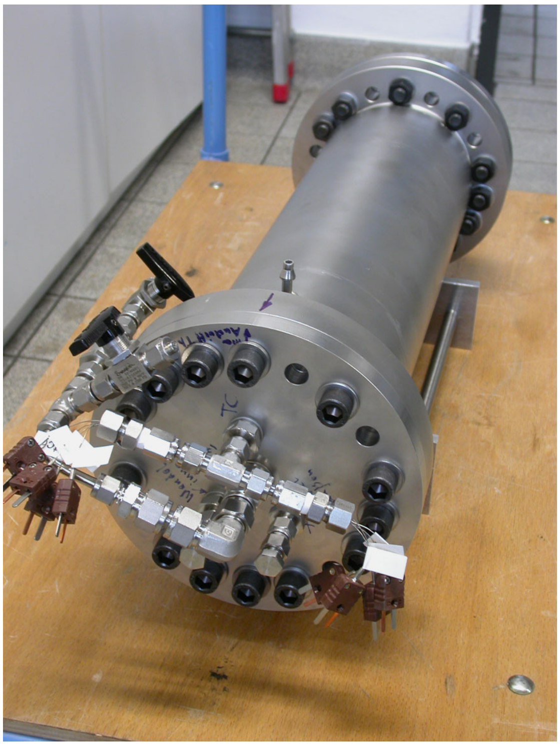

Figure 3: Final version of the hydrogen storage tank.

3 Results

Figure 4 depicts the load profile, hydrogen flow and cumulated electrical energy provided by the fuel cell during one of the experiments. The system was heated up until the fuel cell temperature exceeded 120°C in minute 90 of the experiment time. Subsequently, load cycling was performed on the fuel cell beginning with 206 W, afterwards increased to 235 W and to 240 W, then changed to 190 W, returned to 240 W, lowered to 165 W and finally increased up to 212 W. The hydrogen and the air flow supplied to the fuel cell were adjusted accordingly at the air ratio of 2 before changing the load. Sometimes the load dropped suddenly as can be seen in the figure. This resulted from decreased cell voltage in some cells of the stack. Probably the achieved temperature of the stack was not sufficient for these electrical loads. However after a short time the single cell voltages stabilized and the fuel cell stack began to operate well during the entire testing period. The cumulated electrical energy at the end of the experiment was 660 Wh while the liberated hydrogen mass reached 60 g corresponding to 2.24% of the inserted mass of sodium alanate.

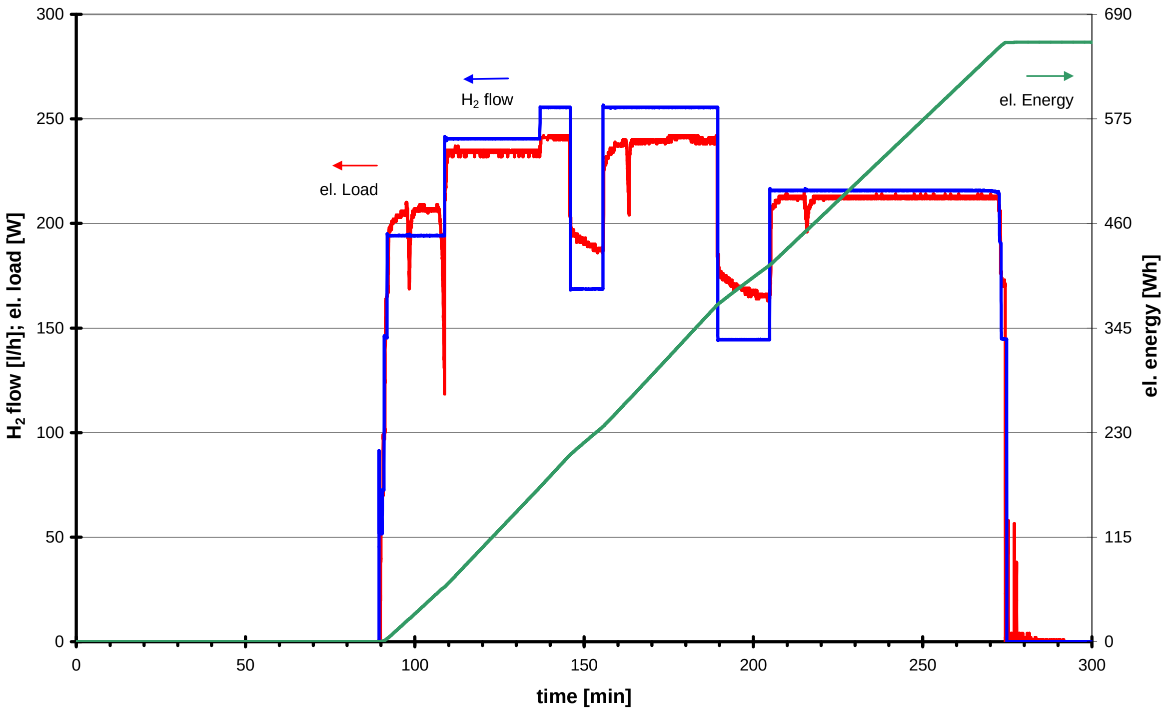

Figure 4: **Load profile, hydrogen flow and cumulated el. energy.**

The development of temperature of the cooling medium and the fuel cell stack is illustrated in Figure 5. Furthermore, the temperature of the oil at the tank inlet\outlet and at fuel cell inlet\outlet and also the temperature of the fuel cell stack are depicted in Figure 5. There is a huge temperature difference between the oil inlet and outlet in the reactor at the beginning of the test because of the mass of the vessel and additional metal hydride that had to be heated up. The maximum of the heat flow in the warm up phase was 1530 W in the tank and 470 W in the fuel cell at approx. 31 kg/h mass flow of the oil. After the thermostat was switched off (90th minute) the oil temperature in tank inlet was decreased sharply because of a sudden loss of auxiliary heat supply.

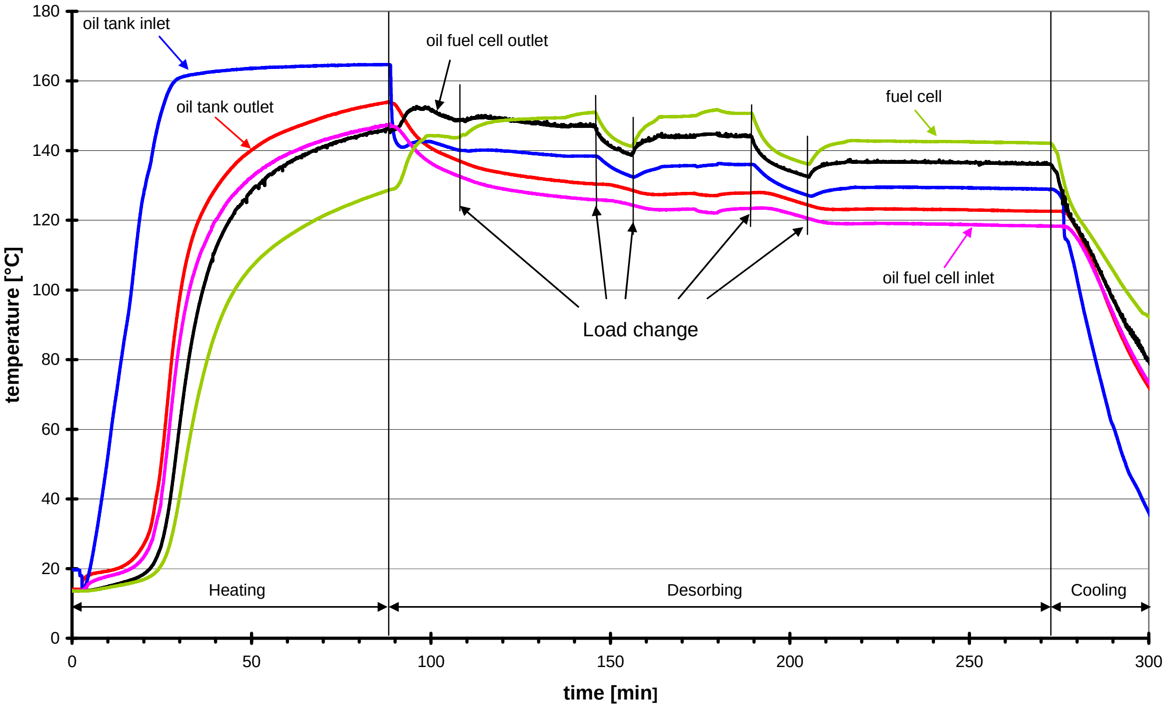

Figure 5: Oil and fuel cell temperature.

From this moment this temperature was lower than the oil temperature in fuel cell outlet, which can be explained by heat losses between both components. A similar trend can be observed between oil temperature in tank outlet and fuel cell inlet. Each time the load was increased, both the temperature of the oil in fuel cell outlet and of the stack increased but the stack temperature rose at bigger ratio and also at the moment, when the oil temperature rise already had stopped. In the stack the generated heat during the operation was therefore transferred both to the cooling fluid and to the housing of the fuel cell. However the temperature in the tank inlet was influenced too, but at lower ratio, because of the heat losses. The pressure in the tank at the beginning of H_2 release reached 77 bar and the temperatures of the sodium alanate were in the range of 136-156°C.

4 Conclusions

A high temperature fuel cell was operated together with a hydrogen storage tank based on complex metal hydride sodium alanate. Both components were thermally coupled so the heat generated by the fuel cell was transferred to the sodium alanate in the hydrogen storage tank for desorbing hydrogen which was then supplied to the fuel cell. The system was operated at different current loads applied to the fuel cell. The temperatures in the thermal circuit followed the loads and although the oil temperature in the tank inlet was approximately 8 K lower than the oil temperature in the fuel cell outlet due to heat losses, 2,24% of hydrogen content of the metal hydride could be liberated during 3 h (in comparison to 3% in the very first cycle). The generated electrical energy was 660 Wh. In comparison to theoretical hydrogen content in sodium alanate of 5,5% the evolved hydrogen amount is lower but the experiment began at relatively low stack and reactor temperatures (128°C and approx. 150°C respectively) and probably during the second reaction step which is more temperature sensitive not the whole amount of hydrogen could be desorbed at the available reaction rate. On the other hand the warm up procedure should not be exceeded because the auxiliary heat source does not really exist in real life technical system and the heat needed for the desorption of hydrogen should only be provided by the fuel cell. In future systems the heat losses in the thermal circuit have to be radically reduced. For example in the last part of the test the heat flow consumed by the tank was 125 W. At the same time the heat dissipated between the fuel cell and the tank was 144 W and between tank and fuel cell on the other side the heat loss was 82 W. Because of the poor thermal conductivity of the sodium alanate (0,6-0,7 W/m*K) [4] the heat transfer is relatively low. It can be improved by increasing the flow of the thermal fluid on the one hand and by increasing the heat transfer area on the other hand [5]. But it should be kept in mind that the heat transfer resistance is primarily offered by the sodium alanate particles.

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