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**complex metal hydride - hydrogen storage of the future**

**BOR4STORE B4S-SM/MM solid-state tank**

first semi-commercial borohydride solid-state hydrogen storage completed

H2-storage > 8 wt.% and > 80 kg H2/m³ in the storage material

Wenden/Olpe, Germany

Consisting of 9 European partners, the Research Group "BOR4STORE" [1, 2] has been able to develop a semi-commercial borohydride solid-state storage tank for the very first time. The consortium in that was to supported over 3.5 years by the European Commission, the Helmholtz-Centre Geesthacht (HZG) has been the coordinator and the corresponding tanks were developed at Zoz at Wenden where this week the model B4S-SM was shipped out.

The B4S-SM insofar represents the single module version of the in objective multi-modular tanks B4S-MM. The is the first fully functional, albeit not yet economic but virtually production-ready LiBH4 storage system and can be ordered at Zoz including all approvals from August 1st, 2016. This technological breakthrough was made possible through the cooperation with the group of Prof. Klassen, Dr. Dornheim, Dr. Bellosta of Colbe, Dr. Taube and Dr. Capurso at HZG, researching for years in the field of reactive hydride composites (RHC) and having already completed first test tanks. The hydrogen loading process in this storage material is completely reversible and the H2-release is thermally activated only.
background:

The entire world is seeking for cost-effective and efficient energy storage systems for fast, clean and large-volume energy storage, particularly for decentralized storing of excess energy and thus being able to provide comprehensive nationwide energy supply and zero-emission mobility. Hydrogen (H2) in that is the most attractive candidate, e. g. to be produced by electricity from solar power or wind turbines and then after a time delay, namely when the sun is not shining or the wind is not blowing, to be utilized e. g. in fuel cells to generate electricity again. For this purpose it is however necessary, to be able to store and again to release H2 economically and effectively [2, 3].

So-called complex metal hydrides [3-5] could foreseeable represent a class of the best hydrogen energy storage of the future. The largest known storage capacity thereby has lithium borohydride (LiBH4), with a theoretical H2-capacity of 18.3 wt-% [6, 7]

\[
2\text{LiBH}_4 \rightarrow 2\text{LiH} + 2\text{B} + 3 \text{H}_2
\]

and thus is approximately 6 times higher than today's known room-temperature hydrides at 2-4 wt-\%. However, for making this potential commercially available, major research efforts are still necessary.

An outstanding contribution to this was provided from April 2012 to September 2015 by the European project consortium BOR4STORE [2], consisting of: HZG - Helmholtz-Zentrum Geesthacht Zentrum für Material- und Küstenforschung GmbH (D), Abengoa Hidrógeno S. A. (ES), Katchem Spol. S. R. O. (CZ), Aarhus Universitet (DK), Institut for Energiteknikk (NO), Università del Studio de Torino (I), EMPA - Eidgenössische Materialprüfungs- und Forschungsanstalt (CH), National Centre for Scientific Research "Demokritos" (GR) and Zoz (D) headquartered at Wend en, Germany.

The "BOR4STORE" project was supported under the European Public-Private Partnership "Fuel Cells and Hydrogen Joint Undertaking" [1] (FCH JU) with approximately 2.1 MioEuro. The objective here was to obtaining a basic scientific understanding of boron based hydrogen storage materials beyond 8 wt-\% capacity as well as the investigation of most cost-effective synthesis and manufacturing possibilities of such materials. As the ambitious goal, a fully functional unit of a solid-state tank including the thermal connection to a SOFC fuel-cell was planned as the project result/demonstrator.

In this project, a lot has been achieved, although e. g. the tank manufacturing was completely underestimated in both, the cost as well as the time to be spent for seemingly as simple things like materials procurement and certification.

So the reactive hydride composite material (RHC) from lithium-boron and magnesium hydride (LiBH4 + MgH 2) with an H2-capacity of about 9 wt-\% [9]:

\[
2\text{LiBH}_4 + \text{MgH}_2 \rightarrow 2\text{LiH} + \text{MgB}_2 + 4\text{H}_2
\]

has been identified as the most promising system. Particularly under the given high sorption-temperature in the range of several 100°C, modelings from structure to thermodynamics were created and phase diagrams designed. Included were also costs analyzes, set-up of a SOFC and the design of two tank systems.

The tank manufacturing was the core task of Zoz where the particular challenges were determined by the combination of high temperature and relatively high pressure, the presence of hydrogen and necessary safety certification.

Due to the completely new findings generated during the project, the cost of 2 planned tanks were found to be much higher than stated in the project application before and also the timeline could not be adhered.
So e. g. as for the procurement of the raw material for the tank shell, it did not take a few weeks but several months before the material finally arrived at Zoz and this special steel could be traced back over 2 continents. To almost a year, the technical inspection by the German TUEV has been delayed, since also here, a completely new chapter had to be opened.

Within the project, both tanks could indeed be completely designed and calculated, however only the detailed design plans of B4S-tanks were insofar the project result:

| ![H2 single-module tank B4S-SM](image1) | ![H2 multi-module tank system B4S-MM](image2) |

Since Zoz in this technology has greatest interest and since the result of the project insofar is the precise know how, how such a tank is to be realized, the single module tank B4S-SM was manufactured after the official end of the project on their own, completed to the end of 2015 / beginning of 2016 and certified by the German TUEV in February 2016.

The B4S-SM tank at about one meter length and a weight of about 25kg is designed for the operation up to 650°C at a maximum load/operating pressure of 100bar with a test pressure of 325bar and stores about 50g hydrogen.

Compared e. g. to the RT-hydride based H2Tank2Go® [10] from Zoz, that at a length of 30cm, a weight of about 4kg at room temperature and at an operating pressure <10bar with a test pressure of 80bar and for just a fraction of the cost, can store more hydrogen, the result seems to be sobering. But it is not ! Zoz to this: “We are here almost at the very beginning of a technology that for stationary and mobile energy storage does offer far higher potentials than room-temperature hydrides, H2-pressure gas systems or electrochemical energy storage / battery - as for today's knowledge - could ever do”.

The B4S-SM-tank "in nearly finished state" was presented during the OZ-16 in March 2016 at Wenden/Germany [11]. Here, also representatives of the BOR4STORE project partners were represented with presentations and as exhibitors: Prof. Wolfgang Kaysser and Prof. Thomas Klassen from HZG, Prof. Andreas Züttel from EMPA as well as the doctoral students Ms. Priscilla Huen and Mr. Seyedhosein Payandeh from Aarhus University and Ms. Anna Wolczyk from the University of Turin. Furthermore, the tank could be already introduced to the "hydrogen world", so also to Dr. Klaus Bonhoff, Managing Director of NOW GmbH, the National Organization for Hydrogen in Germany.
At that time, the control module and interface for the resistance heating system, that is needed for the first tank test operations, was still missing. Meanwhile completed for this at the Zoz headquarters at Wenden (HQH), the tank on last Monday was delivered to HZG that not accidentally entertains the "HZG - Hydrogen Technology Centre, Olpe" inside the Zoz Technology Center (ZTC) at Olpe/Germany. However the charging/loading and further investigation/testing will not be done at Olpe but in Geesthacht. On long term it is planned to provide the temperature of the tank with the waste heat of a high temperature fuel cell (SOFC). At present, a corresponding device is concept at HZG.

The performance characteristics of this first semi-commercially available hydrogen tank based on borohydride reactive hydride composites are given as follows:

<table>
<thead>
<tr>
<th>H2-tank system BOR4STORE - B4S-SM</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>B4S-SM single module tank</td>
<td>B4S-SM &quot;entire system&quot;</td>
</tr>
<tr>
<td>storage material</td>
<td>LiBH4/MgH2 RHC</td>
</tr>
<tr>
<td>H2-Kapazität</td>
<td>~ 50g</td>
</tr>
<tr>
<td>H2 gravimetric RHC</td>
<td>~ 10 wt-%</td>
</tr>
<tr>
<td>H2 volumetric RHC</td>
<td>&gt; 80 kg H₂/m³</td>
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<tr>
<td>insulator</td>
<td>glass fabrics</td>
</tr>
<tr>
<td>tank volume, net</td>
<td>712 cm³</td>
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<tr>
<td>tank weight, net</td>
<td>25,5 kg</td>
</tr>
<tr>
<td>operating pressure</td>
<td>3-100bar</td>
</tr>
<tr>
<td>operating temperature</td>
<td>max. 650°C</td>
</tr>
<tr>
<td>loading pressure</td>
<td>50-60bar</td>
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<tr>
<td>loading temperature</td>
<td>max. 350°C</td>
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<tr>
<td>test pressure</td>
<td>325bar</td>
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<td>certification</td>
<td>AD-2000 (TUEV-Sued)</td>
</tr>
</tbody>
</table>
characteristic absorption cycle (left) and desorption cycle (right) [12]

references:

[12] unpublished measurement data, HZG under kind support of the University of Padua.