PROJECT FINAL REPORT

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4.1.2 Summary description of project context and objectives.

The transition towards a sustainable, carbon-free and reliable energy supply system capable of meeting the increasing energy demand is considered one of the greatest challenges of the 21st century, as expressed e.g. by the 20/20/20 initiative of the European Commission[1]. In order to integrate renewable energy sources (e.g. from sun, wind, and wave energy), being unevenly distributed in location and time, advanced energy storage systems have to be developed. These storage systems have to fulfil the requirements of a **high volume related storage density**, and preferably low weight for portable applications. A **high energy efficiency** is required to keep operating cost as low as possible, and especially not to decrease the overall efficiency of the energy conversion chain from limited resources (e.g. sun in Northern Europe) to the end user.

Storage of electrical energy by converting it to hydrogen allows for superior storage densities of more than 5 – 10 times higher compared to today's advanced Li based batteries, despite the overall lower energy efficiency of the conversion chain. Here storage in metal hydrides is of special interest. They neither require high energy expenses for compression of hydrogen, but only pressures of several tens of bar for tank loading, which can be easily delivered by current state of the art electrolysers. Nor do they require high energy expenses for cooling down to liquid hydrogen temperatures. Additionally, metal hydride based tanks can be constructed without using expensive fibre reinforced carbon hulls, but by using conventional heat exchanger materials like temperature resistant stainless or high strength steels.

Taking into account, that in solid state hydrogen storage at least 50% of weight and volume is needed for balance of plant (BoP, e.g. hull, heat exchanger etc.), for achieving the call targets on weight and volume related system capacities, hydrogen storage materials have to possess theoretical storage capacities of more than 80 kg H_2/m^3 of material volume and more than 8 weight% at least.

Though metal hydrides have been investigated since the early 1970's and again with high effort since the beginning of this century worldwide, still no hydrogen storage material exists today, additionally to capacity, also fulfilling all of the following requirements at the same time:

- Kinetics and temperatures of the hydrogen loading and discharge reactions suitable for the application, for which the storage material is used, e.g. PEM-, HT PEM- or SO-FCs.
- High cycling stability of the storage material, being especially important for stationary hydrogen storage, where several thousands and more of hydrogen loading / discharge cycles are required.
- Cost of the storage materials at an acceptable level of <50 €/kg, allowing for a storage system cost level at or below 500 €/kg of stored H_2.
- Practical proof of the advantage of a solid state hydrogen storage system with respect to cost and energy in a working prototype of a combined fuel cell – solid state hydrogen storage system.

BOR4STORE tackled these challenges by investigating **a new generation of boron hydride based storage materials**. Only boron hydride based hydrogen storage materials exhibit the necessary high hydrogen storage capacities (more than 120 kg H_2/m^3 and up to 18 wt %)[2] among all known hydrogen storage materials suitable for gas phase loading and discharge. They had been investigated in EU projects with respect to synthesising them directly from the elements (NESSHY, FLYHY), understanding reaction mechanisms (NESSHY, COSY, FLYHY), modifying them by anion substitution (FLYHY) or introducing them in nanosized scaffolds (NANOHY). Important steps forward towards fully reversible hydrogen loading had also been made by mixing them with other hydrides in the so called Reactive Hydride Composites (RHC) (COSY). Furthermore, the potential for decreasing dehydrogenation temperatures by partial fluorine substitution and enhancing reaction kinetics by nanoconfinement of the hydrides in nanosized scaffolds had been demonstrated (FLYHY and NANOHY), Significant progress had also been made in the US (e.g. DOE Metal Hydride Center of Excellence) and in Japan (e.g. HYDROSTAR project). But the following **deficits still remained unsolved**:

- **Temperatures for decomposition** at reasonable reaction speeds still were too high (> 350°C) or too low (RT or below RT in the case of "unstable" boron hydrides like $Al(BH_4)_3$ or $Zr(BH_4)_4$), **reversibility** of hydrogen loading was only very limited or impractical in the case of pure boron hydrides, **cycling stability** had either not been tested at all or to just a few cycles only.
- Boron based **materials cost** of several thousand, partially more than 10.000 €/kg were too high for large scale application.
- Use of boron hydride based storage materials in a **practical application** (e.g. to supply a fuel cell), especially with a heat recovery system in order to improve the global efficiency of the tank – application - system, has not been demonstrated yet.

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[1] "The EU climate and energy package", http://ec.europa.eu/clima/policies/brief/eu/package_en.htm

[2] L. H. Rude, T. K. Nielsen, D. B. Ravnsbæk, M. B. Ley, B. Richter, L. M. Arnbjerg, U. Bösenberg, M. Dornheim, Y. Filinchuk, F. Besenbacher, T. R. Jensen *Physica Status Solidi*, *A* 2011, **208**(8) 1754–1773..

To overcome these deficits, it was the objective of BOR4STORE to

- synthesise **novel boron hydride based materials** (e. g. bi- and tri-metal boron hydrides, which can be anion substituted) **and composites** (e.g. Eutectically Melting Composites (EMC)) with high hydrogen storage capacities >8 wt.% and >80 kg H_2/m^3, and evaluate their suitability for practical application in a careful materials downselection process,
- **accelerate reaction kinetics and adjust reaction temperatures** appropriately to supply a SOFC with sufficient hydrogen pressure and flow at acceptable rehydrogenation times of 1 hour or below by systematically investigating additives to understand their effects on rate limiting reaction steps,
- **enhance the cycling stability** of the materials to several 1000 cycles also by suitable **additives** as well as by **scaffolding** the storage material **in pore size optimised porous materials** to tailor reaction pathways, prevent phase separation and retain a high storage density,
- **decrease materials cost** to reach the long term target of < 50 €/kg in large scale production, by (a) developing **cost effective materials synthesis** routes, and (b) systematically investigating the effects of impurities on storage properties to enable the use of more **cost effective raw materials** with less stringent requirements on purity, and
- **demonstrate the suitability, high energy and cost efficiency** of a boron hydride based laboratory prototype tank, containing ca. 100 – 1000 g of storage material, to correspondingly supply a 0.1 - 1 kW SOFC (exact power was to be decided in the course of the project) as a model for a continuous power supply for specific applications like net independent telephone or weather stations, backup power for lighting and control, CHP, potentially being also a model for APU's for trains or ships and other portable applications.

Deliverables of the project were defined as

- a novel solid state hydrogen storage prototype system based on boron hydrides, with system **capacity > 4 wt.%, and > 40 kg H_2/m^3,** with materials reaction enthalpies and **kinetics** of hydrogen loading and discharge suitable for integrating it with a SOFC, with tested cycling stability >98% of retained capacity over at least 500 loading-unloading cycles,
- **cost effective production** routes of the materials, with demonstrated potential for scale-up and for reaching **a system cost of 500 €/kg of stored H_2**,
- a laboratory **prototype of a 0.1 - 1 kW SOFC integrated with a 0.1 - 1 Nm^3 hydrogen storage system** for continuous energy supply with significantly improved storage capacity and overall energy efficiency compared to compressed gas storage and other fuel cell technologies, respectively.
- an indicator of **allowable hydrogen purity** for stable storage properties,
- **Techno – economical evaluation** of the scaled prototype (in connection to the aforementioned applications.

The major innovative idea of BOR4STORE which was expected to bring the project beyond the present state-of-art was the use of an integrated, holistic approach in synthesising novel boron based materials, which exhibit high weight and volume related capacities of of 8 to 18 wt% and up to 120 kg H_2/m^3 and hydrogen release temperatures below 450°C. The nature of this approach is to systematically combine innovative features (such as composite synthesis, ionic substitutions, use of scaffolds and additives etc.), thus also building on and rationalising the findings of previous projects. This efficient approach was used to screen a large range of materials, and optimise the most promising, thus bringing the project beyond the present state-of-the-art. Materials which were investigated included:

- unstable and stable **(**at RT) **boron hydrides** extending experiences from FuncHy, NESSHY, COSY and FLYHY projects,
- **composites** of these boron hydrides with other hydrides, i.e. RHC (employing experiences from FuncHy and COSY projects) and EMC of boron hydrides, allowing for tailored reaction enthalpies and enhanced rehydrogenation kinetics and reversibility (thereby extending experiences from COSY and SSH2S projects),
- **chemical modifications** of the aforementioned storage materials by **anion and cation substitution**, respectively, to achieve appropriate reaction enthalpies suitable for the envisaged application of integrating with a SOFC (using experiences from FLYHY project), and
- **hydrogen storage materials confined in pore size optimized scaffolds** to enhance reaction kinetics and cycling stability with acceptable trade-offs on hydrogen storage densities (using experiences from NANOHY)

BOR4STORE exploited the potentials to manipulate the reaction pathways by performing **fundamental investigations on the mechanisms for hydrogen release and uptake** in the boron hydride based materials in order to **optimise their kinetic properties, to tailor reaction enthalpies and reaction pathways** and thus, to tap the full potential of these materials. Reaction **kinetics and reaction pathways should be tailored by suitable additives** as well as by **optimised reaction temperatures and hydrogen pressures**. **Scaffolding in pore size optimised porous materials** were to be employed to enhance reaction kinetics while retaining as high a storage capacity as possible by using the minimum necessary amount of the scaffold. The influence of purity of the storage material were to be systematically investigated, as well as novel routes for cost effective materials synthesis, with the target of **showing the potential to decrease cost of the storage systems** to the target value of the call. Thus it was expected to be possible to achieve acceptable fast hydrogen loading and unloading as well as to prevent decrease of storage capacity by unwanted side reactions and reaction end products. During the runtime of the project by a **careful materials downselection process** the most promising materials were selected. The most promising was then to be tested in the prototype hydrogen storage - SOFC system. This, together with the data on routes for cost effective materials production, were expected to give **data for the overall energy and cost efficiency** of the developed storage material and tank system.

In order to achieve the targets described above, it was the overall strategy of BOR4STORE to:

1. identify most promising materials through a careful downselection process based on quantitative criteria for capacity, enthalpy, kinetics, release of non-hydrogen gases, cycling stability, and cost,
2. optimise reaction kinetics and cycling stability, to achieve proper hydrogen loading and discharge properties for the envisaged application,
3. find cost effective sources for raw materials and routes for their processing, investigate the effect of impurities on capacity, reaction kinetics and cycling stability, and find acceptable levels to achieve the targets on hydrogen capacity and cost,
4. evaluate the achieved progress in materials properties in a prototype test system of a SOFC integrated with the hydrogen storage tank.

Based on this overall strategy the following work packages had been defined:

WP1 encompasses the **essential steps for development of novel boron based materials**, extending results of STORHY, NESSHY, COSY and FLYHY projects. Materials were subject to the downselection process as described in WP4.

WP2 was dedicated to **in depth investigations of the effect of additives and of scaffolding** on selected boron based materials produced in WP1 with the target to optimise their reaction kinetics and cycling stability, as required by supplying a SOFC for stationary applications.

WP3 especially focused on **modelling of crystal structures and experimental data (IR, NMR, hydrogenation pathways) by *ab initio* and CALPHAD calculations, and on the effects of additives in boron compounds** in order to give hints and achieve understanding for special additives and their effects on critical reaction steps.

WP4 evaluated sources for **cost effective raw materials** and studied their hydrogen sorption properties with emphasis on acceptable levels of impurities. Based on the work of WP1 a **competitive materials processing technology** up to the kg labscale was to be developed and the potential for reaching the cost target of the call for proposals evaluated. The task of **materials downselection** (also for WP1 and WP2) was part of WP4 in order to assure proper assessment not only of materials technical properties, but also cost, aiming to focus on and in the end select most promising systems for WP5.

WP5 Based on **thermo-chemical modelling of the hydrogen storage tank** and a **simulation of the whole SOFC – hydrogen storage tank system**, a **laboratory prototype** of such a system was to be constructed. The system should contain sufficient hydrogen to supply an 1 kW SOFC at suitable pressures and H_2 flows. The system should be tested with respect to hydrogen loading and unloading characteristics, cycling stability and sensitivity to hydrogen quality under parameters simulating envisaged applications. The obtained data on the performance and the total energy efficiency of the system should allow for judging the achieved technical progress with respect to hydrogen storage properties well as to estimate the **economics of hydrogen storage systems and benchmarking** them against competing technologies like compressed or liquid hydrogen storage.

WP6 was dedicated to **management** of project work, reporting, handling intellectual property rights and **dissemination** of the project results from raising public awareness up to preparation of a final project summary report and a report on utilisation potentials of the project results, to be made available to the public.

The following report on the main S&T results and foreground, developed in BOR4STORE, is structured along the work in work packages 1 to 5.

4.1.3 Main S&T results/foregrounds

4.1.3.1 Work packages 1 and 2: Materials Synthesis and Characterisation, Materials optimization: reaction pathways, kinetics and cyclability

Objectives of the work packages

WP1 and WP2 aimed at synthesis of new boron hydride based high capacity hydrogen storage materials with high reliability, reproducibility and safety and thermodynamic properties compatible with the target of supplying a SOFC, identifying rate limiting steps in the hydrogenation reactions and investigating additives and confinement in nanosized scaffolds to improve reaction kinetics and cycling stability. With a focus on cost effectiveness, BOR4STORE employed the routes of wet chemical synthesis (AU, KAT), Reactive high energy milling (RHEM) (HZG, AU, IFE, Empa, Zoz), combinations of wet chemical synthesis, RHEM and gas-solid reactions (AU, HZG, IFE, Empa, Zoz, KAT), and plasma treatment of educts for hydride synthesis from selected elements and compounds (Empa).

Structure-composition-property relationships were established, assisted by theoretical calculations on the design of new materials, in WP3. As the number of materials planned to be investigated in WP1 was considerably large, the storage materials were subjected to a rigorous downselection process, performed in WP4, Task 4.1., solely, resulting in a stop of the work on materials, not fulfilling and not having any future potential to fulfil the downselection criteria.

Task 1.1: Synthesis of pure boron hydride based storage materials (KAT, AU, IFE, UNITO, Empa)

(i) Synthesis of pure bulk, oxide, borate and halide free boron hydride polymorphs (AU)

All the standard metal boron hydrides can be synthesised by means of using two distinct methods of synthesis developed at AU. Direct control of specific polymorphs obtained is an important point to make, when considering the significantly varying characteristics displayed by e.g. α– and γ-$Mg(BH_4)_2$. We have demonstrated the preparation of specific polymorphs by post-synthesis treatments, i.e. variation of pressures, temperatures and duration of treatment. Optimizations of the reactions have been undertaken and ideal conditions have been established. A general protocol of purification of products has been established and is included as a useful addition to the method. The method has potential for reducing costs of boron hydride production since *one* source of increased costs can be cut: the commercially available metal hydrides. Hydrogenating metals of the relevant materials for production of non-commercial metal hydrides appears to be cheaper than buying the commercially available versions in gram scale quantities. Furthermore - many metal hydrides are not commercially available, thus producing these within the consortium has been the only option (e.g. YH_3).

(ii) Synthesis of novel Boron Hydrides

A range of new boron hydrides has been synthesized in BOR4STORE. A few examples are given below.

A novel method for the preparation of $Mn(BH_4)_2$ was completed in BOR4STORE. The metathesis of $LiBH_4$ and $MnCl_2$ in toluene/dimethylsulfide (DMS) solvent at *RT* yields a mixture of LiCl and $Mn(BH_4)_2$ which is extracted in DMS to form the solvate $Mn(BH_4)_2\cdot½DMS$. Removal of the coordinated solvent provides the α-$Mn(BH_4)_2$ polymorph. Removal of coordinated DMS under alternative circumstances has been shown to yield a supposedly nano-porous form of $Mn(BH_4)_2$ denoted γ.

A solvate containing boron hydride, $Y(BH_4)_3\cdot S(CH_3)_2$, provides the α-$Y(BH_4)_3$ polymorph upon desolvation at elevated temperatures in vacuum. The material is phase pure, and is completely free of halides, borates or oxide impurities [[3]].

At AU, a method using vapour deposition of molecular boron hydrides was successful for the synthesis of $Zr(BH_4)_4$.[4] Ball-milling $AlCl_3$ with $LiBH_4$ gives $Al_3Li_4(BH_4)_3$, which decomposes spontaneously into aluminum boron hydride and decomposition products such as diborane and hydrogen at room temperature. First attempts to stabilize the compound by adsorption on carbon scaffolds did not show a significant effect. $Ti(BH_4)_3$ is formed by the solid-state reaction of $LiBH_4$ with $TiCl_3$. It decomposes spontaneously at room temperature (similarly to $Al(BH_4)_3$) into Ti, B_2H_6, and hydrogen. Due to the difficulties in handling these unstable materials, the activities on producing composites with more stable boron hydrides were decided to be stopped in the project.

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[3] Morten B. Ley, Mark Paskevicius, Pascal Schouwink, Bo Richter,a Drew A. Sheppard, Craig E. Buckley, Torben R. Jensen, *Novel solvate phases $M(BH_4)_3$ × $S(CH_3)_2$ (M = Y, Gd) and properties of salt-free $Y(BH_4)_3$*; *Dalton Trans.*, **2014**, *43*, 13333. (**DOI**: 10.1039/C4DT01125B)

[4] Line H. Rude, Marta Corno, Piero Ugliengo, Marcello Baricco, Young-Su Lee, Young Whan Cho, Flemming Besenbacher, Jacob Overgaard and Torben R. Jensen, *Synthesis and structural investigation of $Zr(BH_4)_4$*, J. Phys. Chem. C 2012, 116, 20239−20245.

(iii) Industrial synthesis of boron hydrides

Cost effective synthesis of $LiBH_4$. - Metathesis of LiBr and $NaBH_4$ (AU)

The lowest limit of costs for boron hydrides is essentially dictated by the costs of $NaBH_4$ (~ 25 €/kg according to Katchem) which in all cases is the denominator for borane supply costs, because it is the very principal source of all borane - for gas (diborane production) or for other metal boron hydrides (metathesis reactions), or as organic borane complexes (e.g. dimethylsulfide borane complex). Thus $LiBH_4$ has been synthesized from $NaBH_4$ and LiBr (world market price ca. 30 – 50 €/kg), following a literature protocol. [[5]] This method could very well constitute a more cost effective route to $LiBH_4$ since the starting materials are significantly cheaper than those used in the methods described above. The costs for $NaBH_4$ and LiBr are comparable (~ 25 €/kg and 30 – 50 €/kg, respectively) and the ether solvent can be recycled in an effective industrial setup. Taking beforementioned raw materials cost and just adding the necessary amounts of materials, in order to produce 1 kg of $LiBH_4$, 1,737 kg $NaBH_4$ and 3,987 kg of LiBr are necessary, leading to pure materials cost only of ca. 203 €/kg of $LiBH_4$, but not including necessary purification, recycling of the ether solvent etc.

New routes for industrial synthesis of Boron Hydrides - New routes for $Ca(BH_4)_2$ and $Mg(BH_4)_2$ (KAT)

For preparation of $Ca(BH_4)_2$, Kat focused on two different “wet“ chemistry synthesis methods The first methods are solvent free addition reactions, in which borane-complexes are used as a source of boron. The second one is a metathesis reaction in THF (C), where $NaBH_4$ is used. In this new approach the more reactive dimethylsulfide borane-complex (DMS) was used, in particular in case of isotopically labelled material. The main advantage of this new synthesis route is the use of lower reaction temperature in comparison with the published reactions and thus preventing the formation of larger boron clusters, namely *closo*-decaborate and *closo*-dodecaborate anions. We obtained calcium boron hydride by using this approach in relatively high yield with a purity over 90% and in a larger quantity (150 g in one batch) in slightly lower yield and comparable quality. As an alternative method for the preparation of calcium boron hydride, especially for isotopically enriched boron hydrides, we used the well-known metathesis reaction of sodium boron hydride and calcium chloride in THF (method C) and obtained calcium boron hydride by using method C in average yield with purity over 90%. By using both methods we successfully prepared isotopically enriched boron hydrides in good yield and purity.

For preparation of $Mg(BH_4)_2$, Kat also focused on the synthesis by wet-chemistry routes. In an addition reaction the more reactive dimethylsulfide borane-complex ($BH_3{\cdot}DMS$) without presence of strongly coordinating solvent was used. The advantage of this new route is the lower reaction temperature (80 °C) in comparison with the published methods (160 °C), thus preventing the formation of larger boron clusters (such as $[B_9H_{14}]^-$, $[B_{10}H_{10}]^{2-}$, $[B_{11}H_{14}]^-$, $[B_{12}H_{12}]^{2-}$). By using this approach, we obtained magnesium boron hydride in relatively high yield with purity over 90% and also in larger quantity (100 g in one batch) in comparable yield and quality. Due to availability of the isotopically labelled starting materials (^{10}B, ^{11}B or D), this route is useful for synthesis of isotopically enriched boron hydrides, too, [i.e. $Mg(^{10}BH_4)_2$, $Mg(^{11}BH_4)_2$ or $Mg(^{11}BD_4)_2$] in good yield and purity.

Task 1.2: Synthesis of boron hydride based composite storage materials (AU, IFE, UNITO, Empa)

(i) ^{11}B MAS NMR investigations on different samples of the system “$Ca(BH_4)_2$-Mg_2NiH_4” Reactive Hydride Composite (UNITO, HZG)

$Ca(BH_4)_2$-Mg_2NiH_4 is the first $Ca(BH_4)_2$ based mixture with an effective boron transfer to the other component in the mixture resulting in the formation of the ternary boride $MgNi_2$-$5B_2$. This represents a promising approach to create a reactive composition with lower enthalpy of desorption. The NMR measurements provided highly relevant insights into the composition of various samples at different sorption states. Using this additional information it has been possible to deduce the reaction paths of the system.

(ii) Composites containing two or three stable metal boron hydrides (AU, IFE)

$Mn(BH_4)_2$ has been mixed with $LiBH_4$, $NaBH_4$ and $Mg(BH_4)_2$ forming new composites for hydrogen storage. All compositions hold high gravimetric hydrogen contents >9 wt.%, and as such are very interesting candidates for hydrogen storage materials.

(iii) New eutectically melting composites (AU, Empa)

Mixtures of $LiBH_4$ and $Ca(BH_4)_2$ or $Mg(BH_4)_2$ have been synthesized by ball milling and were investigated by mass spectroscopy, differential scanning calorimetry, and photography during thermal ramping[6]. Both mixtures displayed eutectic melting behaviour below that of the mono-metallic phases (up to 167 °C lower). The eutectic melt allowed for hydrogen release at temperatures lower than that of the individual components.

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[5] H. C. Brown, Y. M. Choi, S. Narasimhan, Convenient procedure for the conversion of sodium boron hydride into lithium boron hydride in simple ether solvents, Inorg. Chem. **1981** 20, 4456-4457. (**DOI:** 10.1021/ic50226a091)

[6] Mark Paskevicius, Morten B. Ley, Drew A. Sheppard, Torben R. Jensen and Craig E. Buckley, “Eutectic Melting in Metal Borohydrides“, *Phys. Chem. Chem. Phys.*, 2013, Accepted.

Task 1.3: Synthesis of modified composite boron hydrides (HZG, AU, IFE, UNITO)

(i) Anion substituted materials including minor to moderated amounts of amide/imide NH2–/ NH2– (HZG)

In preparation of studies on boron hydrides, to be modified by ammonia containing compounds, the interaction between ammonia gas and alkali-alkali earth metal hydrides was studied. The synthesis of amides of the respective hydrides was possible for all the investigated material except for CaH_2, where the formation of the imide was obtained instead. This study showed for the first time the successful *in situ* SR-PXD analysis of solid-gas reactions using NH_3 as reactive gas. In a second step towards ammonia modified Reactive Hydride Composites, the *in situ* synchrotron radiation powder X-ray diffraction study (SR-PXD) of the ammonolysis reaction of selected alkaline and alkaline earth metal hydrides (i.e. LiH, NaH, KH, MgH_2 and CaH_2) was performed for the first time. The results of this work give new important insights into the formation of metal amides and imides starting from the corresponding metal hydrides. Our results indicate that the formation of the γ-MgH_2 is a key step in the synthesis of $Mg(NH_2)_2$ at low temperature (e.g. via ball milling technique).

(iii) Novel tri-metal boron hydrides (AU)

Novel trimetallic boron hydrides in the systems Li-*M*-Zn-BH_4 (*M* = Mg, Mn) have been synthesized. Unfortunately, these compounds tend to decompose irreversibly by formation of the more stable boron hydrides and reduction of zinc to the metallic state[7]. Therefore work on this type of compounds was stopped .

Task 2.1. Identification of rate-limiting steps (HZG, AU, IFE, UNITO, Empa, NCRSD)

(i) γ-$Mg(BH_4)_2$ (AU, EMPA, IFE,UNITO)

Decomposition and rehydrogenation of $Mg(BH_4)_2$ in mild temperature (200-285°C) and pressure (up to 150 bar) ranges was studied. As it is shown on Figure 1, desorption can be completed in 18-24 hours, and 90% is achieved in at least 10 hours, if decomposed at 265-285°C. Re-absorption of up to 2.2 wt% hydrogen with promising kinetics can be achieved at the pressures > 100 bar. As it was found at UNITO (PCIs at 268-276°C), absorption at pressures ≤ 100 bar results in very slow kinetics and low hydrogen uptakes (ca. 1wt%).

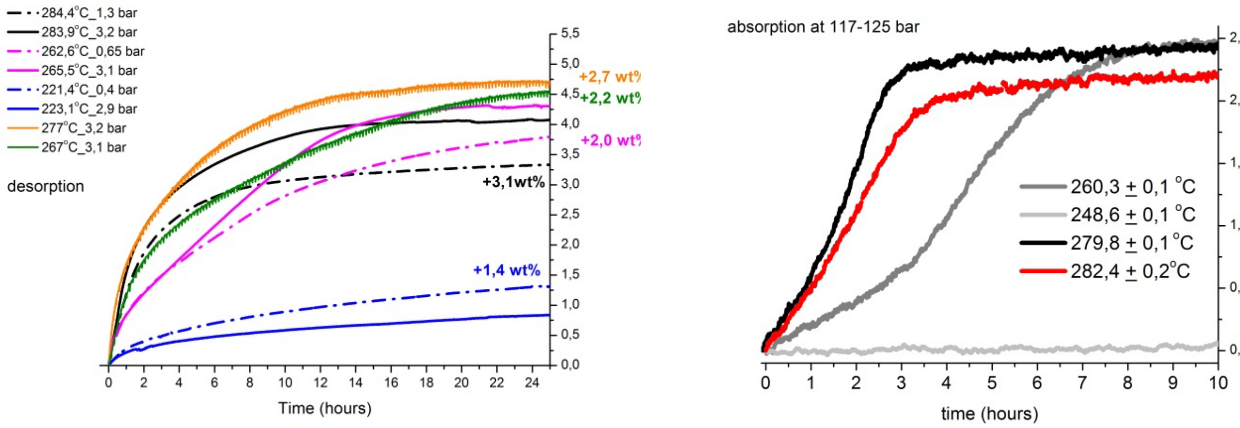

Figure 1 Desorption and absorption isotherms of $Mg(BH_4)_2$. Orange and green desorption curves are measured at UNITO, other curves are measured at IFE. Numbers indicate amount desorbed during heating (at non-isothermal conditions).

The kinetics of H_2 desorption and absorption in $Mg(BH_4)_2$ is significantly increased after ball-milling of the material. >90% is desorbed from the ball-milled sample in 5h (vs.10 in non-ball-milled sample), and re-absorbed in 1h (vs. 5) at 280-285°C.

For investigation of the reaction rate-limiting steps, isothermal kinetics has been modelled using common solid-state reaction models (c.f. WP3, Task 3.3). The desorption reactions follow complex reaction pathways. Absorption reactions fit the models better. Jonson-Mehl Avrami (JMA) analysis has shown that in non-ball milled samples the absorption reactions are limited by diffusion at the beginning, and by nucleation at a constant rate and diffusion-controlled growth at the second stage. On the contrary, the absorption isotherm of the ball-milled sample can be fit to one model throughout most of the reaction with nucleation at a constant rate and diffusion as rate-limited steps. Apparently, ball-milling of pure material enhances the kinetics of hydrogen sorption through enhancing the diffusion.

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[7] Radovan Černý, Pascal Schouwink, Yolanda Sadikin, Katarina Stare, Ľubomír Smrčok, Bo Richter, Torben R. Jensen, Trimetallic boron hydride $Li_3MZn_5(BH_4)_{15}$ (M = Mg, Mn), two weakly interconnected frameworks, *Inorg. Chem.*, 2013, *52*, 9941−9947.

(ii) α–Mn(BH$_4$)$_2$ (borate, halide and oxide free) (AU)

α-Mn(BH$_4$)$_2$ synthesized at AU[8] has been characterized and reaction pathways studied in detail. This material is a very interesting member of the boron hydride family, due to even lower decomposition temperatures than e.g. Mg(BH$_4$)$_2$ with which it is very often compared. The one step decomposition releases a mixture of hydrogen and diborane in a relative ratio of approximately 12-15:1 in favour of H$_2$.

(iii) LiBH$_4$-MgH$_2$-Al RHC (AU)

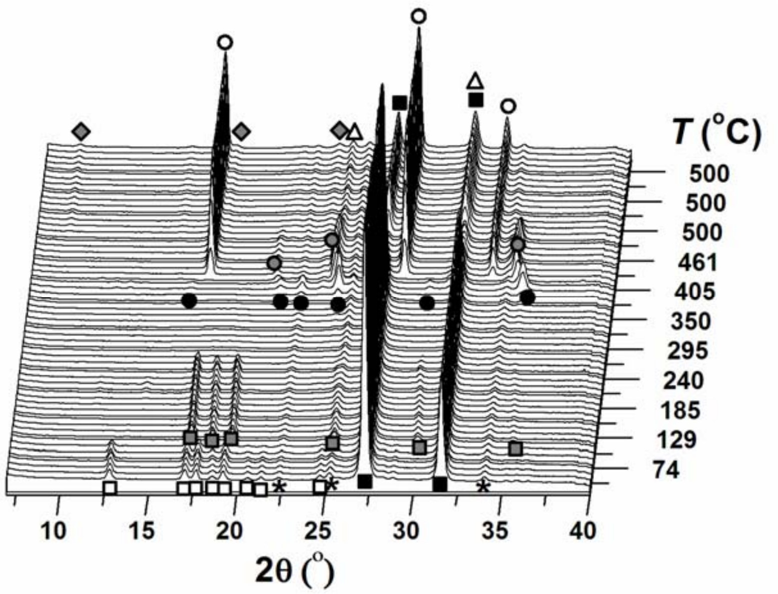

Figure 2 In situ SR-PXD desorption measurement for LiBH$_4$–Al (2:3) in the temperature range from RT to 500 °C, at p(H$_2$) = 10^{-2} bar (ΔT/Δt = 10 °C/min, λ = 1.10205 Å). The temperature was maintained at 500 °C for 15 min. Symbols: □ o–LiBH$_4$, ▨ h–LiBH$_4$, ✱ WC, ■ Al and LiH, ● 1, ◉ 2, △ Li$_x$Al$_{1-x}$B$_2$, ○ LiAl, ◆ 3.

Decomposition pathways in LiBH$_4$-Al (2:3 molar ration) and LiBH$_4$-MgH$_2$-Al (4:1:1 and 4:1:5) are complex and occur through multiple steps in all three samples. *In situ* SR-PXD has shown that during decomposition (Figure 2) of all three samples LiBH$_4$ undergoes its usual phase-transformation and melting at 110-250°C, which was also confirmed by DSC study (Figure 3).

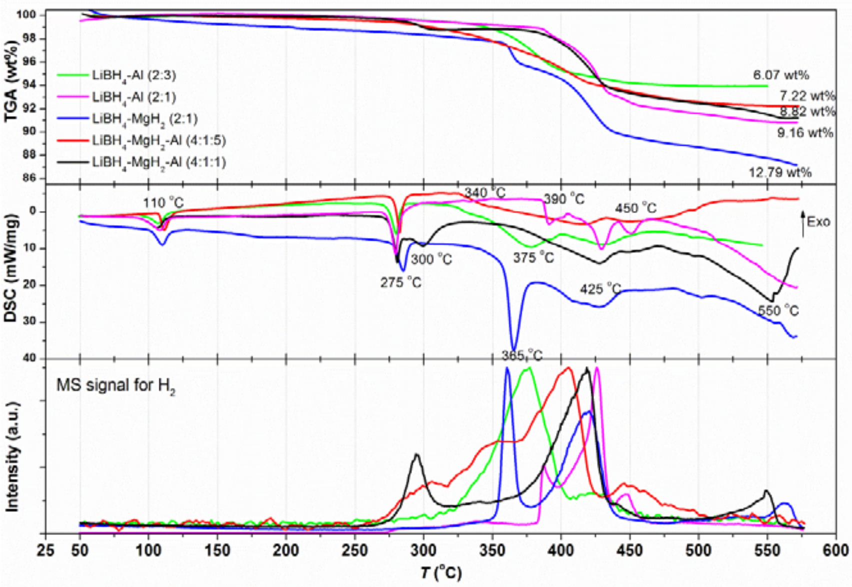

Figure 3 TGA-DSC-MS profiles for LiBH$_4$-Al (2:1), (2:3), LiBH$_4$-MgH$_2$ (2:1) and LiBH$_4$-MgH$_2$-Al (4:1:1) and (4:1:5) in the temperature range RT to 575 °C (5 K/min). The samples were heated under an Ar-flow of 50 mL/min.

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[8] “*Mn(BH$_4$)$_2$; Salt-Free Synthesis and Thermal Decomposition Pathways*”, Poster MH2012; Bo Richter, Dorthe B. Ravnsbæk, Yaroslav Filinchuk, Torben R. Jensen (manuscript in progress).

(iv) Ca-RHC (HZG)

The reduced reversibility of $Ca(BH_4)_2$ is due to the formation of stable boron containing phases such as $CaB_{12}H_{12}$ and amorphous boron. Seeking to shade some light on the reversibility issue of $CaB_{12}H_{12}$ an *in situ* SR-PXD investigation at high hydrogen pressure and temperature was performed on the mixture $CaB_{12}H_{12}+CaH_2$. This study may reveal a new decomposed state by stopping the dehydrogenation, which may more readily be hydrogenated. At the 3rd BOR4STORE meeting $Ca(BH_4)_2$ was excluded from further deeper investigations. Therefore further studies of Ca-based boron hydrides have to be left to the future.

(v) EMC systems: MBH_4-$Mg(BH_4)_2$, MBH_4-$Mn(BH_4)_2$ and MBH_4-$Mg_{1-x}Mn_x(BH_4)_2$, M = Li, Na, K, (AU)

$Mn(BH_4)_2$-$LiBH_4$ (1:1), $Mn(BH_4)_2$-$NaBH_4$ (1:1), $Mn(BH_4)_2$ – $Mg(BH_4)_2$ (1:1)

$Mn(BH_4)_2$ decomposes at relatively low temperatures but is accompanied by the undesired release of diborane.[9] In the eutectically melting composite (EMC) systems with $LiBH_4$ and $NaBH_4$, it was found that the composites exhibit slightly lowered decomposition temperature compared to pure $Mn(BH_4)_2$ and the relative quantities of hydrogen and diborane in the desorbed gases are altered in favour of hydrogen. No reaction between $LiBH_4$ and $Mn(BH_4)_2$ occurs. The EMC with $NaBH_4$ has more complicated decomposition pathway, $NaBH_4$ being significantly consumed at 125°C, during the main hydrogen release step. As temperature increases further, any leftover MBH_4 decomposes as normal. Mixing $Mg(BH_4)_2$ with $Mn(BH_4)_2$ results in a solid solution, MgxMn1-x$(BH_4)_2$ (x = 0 – 0.8) decomposing at much lower temperature than pure $Mg(BH_4)_2$, without severely reducing the hydrogen capacity.[10] The TGA and DSC show a decomposition of the $Mn(BH_4)_2$ – $Mg(BH_4)_2$ composite at already 111 °C, but accompanied by the "usual" release of diborane.

For these three composites, the main objective should not be to lower the decomposition temperature, since this is already very practical. The main issue is the accompanying diborane, being a detrimental effect depleting the material itself. The alteration/fine-tuning of the decomposition reaction should revolve around avoiding diborane release and to reverse this reaction.

$NaBH_4$-$Mg(BH_4)_2$ system

The eutectic mixture of $NaBH_4$ and $Mg(BH_4)_2$ appears to be eutectic in compositions MgNa 1:2 ⇔ MgNa 1:1 as can be seen in the DSC. The endothermic events observed for both MgNa 1:1 and MgNa 1:2 at T = 210-220 ˚C are probably related to the polymorphic phase change of α- to β-$Mg(BH_4)_2$ and the eutectic temperature. Indeed, the *in situ* SR-PXD experiment supports this assumption as the polymorphic phase change occurs at T = 200 ˚C and the peaks of β-$Mg(BH_4)_2$ disappear hereafter. Some doubt as to when the eutectic appears is present, however; thermophotographic experiments do not clearly show if the sample melts. This must to be fully assured and more experiments are underway to establish this.

Task 2.2 Kinetic effects of additives on identified rate limiting reaction steps (HZG, ZOZ, AU, IFE, UNITO, Empa, NCRSD)

(i) Effect of cobalt additives on hydrogen sorption kinetics in γ-$Mg(BH_4)_2$ (IFE)

The effect of 2 mol% cobalt-containing additives (Co_2B, CoF_2, CoF_3) on hydrogen sorption in $Mg(BH_4)_2$ was studied. Combined DCS-TGA analysis has shown that the sample milled with CoF_2 has similar behaviour to milled pure $Mg(BH_4)_2$ (weight loss ca.11 wt%). On the other hand, the samples containing Co_2B and CoF_3 had also similar to each other and different to pure $Mg(BH_4)_2$ behaviour. 8 wt% loss and the disappearance of the first phase-transition peak were observed for these samples in the DCS-TGA. It was found that the investigated CoF_3, Co_2B and $CoCl_2$ additives have minor effect on the kinetics of hydrogen sorption in $Mg(BH_4)_2$. In fact, the most prominent increase of desorption and absorption kinetics is achieved by only ball milling.

(ii) Ca-RHC : $CaB_{12}H_{12}$ + $5CaH_2$ (HZG)

The effect of the addition of Cosan (Cobaltocarborane Sandwich Anion, COSAN, trivial name of Cesium bis(1,2-dicarbollide) cobaltate, $Cs^+[Co(C_2B_9H_{11})_2]^-$) and Fesan (compound comparable to COSAN, but with Fe instead of Co) to $Ca(BH_4)_2$ on its sorption properties and the possibility of hydriding the mixture $CaB_{12}H_{12}$ + $5CaH_2$ was investigated. $Ca(BH_4)_2$ (90% purity), $CaB_{12}H_{12}$ (88% purity), COSAN and FESAN were synthetized by Katchem, CaH_2 (98% purity) was purchased from Alfa Aesar. *In situ* SR-PXD and desorption kinetics measurements showed almost identical reaction pathways of the composites with both additives and similar to that of pure $Ca(BH_4)_2$. DSC-TGA measurements have also shown similar decomposition profiles but T_{dec} in the samples with additives shifted from 325°C to 290°C with respect to pure $Ca(BH_4)_2$.

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[9] S.-I. Orimo, Y. Nakamori, A. Züttel, Materials Science and Engineering B 108 (**2004**) 51–53.

[10] M. Paskevicius, M.P. Pitt, C.J. Webb, D.A. Sheppard, U. Filsø, E.M. Gray, C.E. Buckley, J. Phys. Chem. C 116 (2012) 15231.

Task 2.3 Optimisation of materials stability using using additives (HZG, AU, IFE, UNITO, Empa, NCSRD)

(i) Effect of cobalt additives on hydrogen sorption cyclability in γ-Mg(BH$_4$)$_2$ (IFE)

An ATR-IR study was performed so far on the decomposition and rehydrogenation products on the Mg(BH$_4$)$_2$ with cobalt additives. There was no notable differences with respect to the reaction products of pure Mg(BH$_4$)$_2$. X-ray absorption spectroscopy (XAS) at the Co K-edge was performed on the Mg(BH$_4$)$_2$ ball milled with the additives. Results suggest that Co$_2$B remaines almost unchanged upon ball-milling, first desorption, first absorption and the 3rd absorption of Mg(BH$_4$)$_2$. CoF$_3$ was found to change after ball-milling already. It undergoes further changes upon the first desorption, and then remains almost unchanged upon cycling.

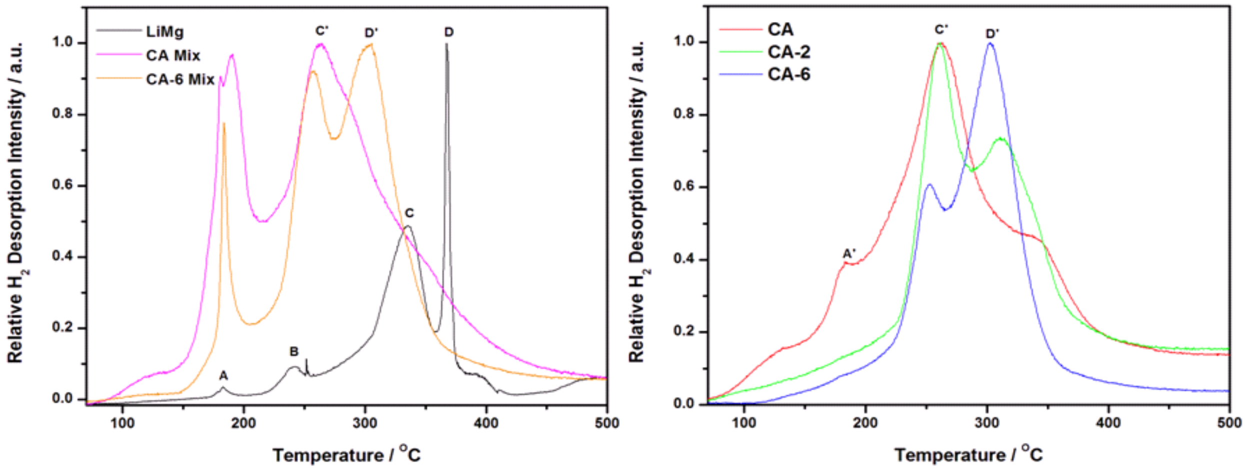
(ii) Effect of CuF$_2$ and CoF$_3$ on gas release in Mg(BH$_4$)$_2$ (IFE)

The effect of CoF$_3$ and CuF$_2$ on gas release was studied by means of TPD-MS. Comparing to pure Mg(BH$_4$)$_2$, we found that: 1) CoF$_3$ does not have a significant effect on the amount of released hydrogen; 2) Sample with CuF$_2$ released less hydrogen at the RT-220°C range, but more in the 220-280°C range; 3) Sample with CoF$_3$ significantly reduced the amount of released diborane, whereas 4) CuF$_2$ on the contrary increased the release of B$_2$H$_6$; 4) both samples released small amount of BF$_3$ gas.

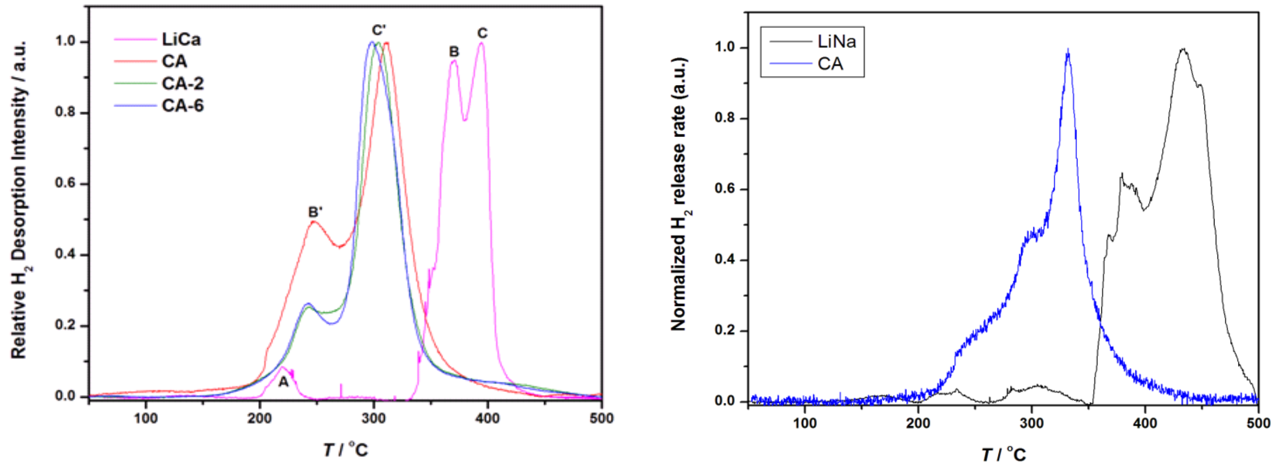
(iii) Effect of CoF$_3$ on gas release in Mg(BH$_4$)$_2$ (EMPA)

IR-TG-MS study of γ-Mg(BH$_{4)2}$+CoF$_3$ decomposition in hydrogen flow has shown 1,6-2,5% weight loss due to diborane. Pure ball-milled Mg(BH$_{4)2}$ has shown 1,9 wt% loss due to diborane.

Task 2.4 Optimisation of materials cycling stability and further properties by using confinement in pore size optimised scaffolds (HZG, AU, IFE, Empa, NCSRD)



a) LiMg composite: bulk (black), physical mixed (pink & orange) and melt infiltrated into CA (red), CA-2 (green) and CA-6 (blue) carbons



b) LiCa composite: bulk (pink) and melt infiltrated into CA carbons

c) LiNa composite: bulk (black) and melt infiltrated into CA carbon (blue)

Figure 4 Normalized H$_2$ desorption intensities as a function of temperature for different EMC as bulk and melt infiltrated into different carbon aerogels (CA)

AU and NCSRD groups investigated the effect of nanoconfinement on the decomposition of Eutectically Melting Boron hydride Composites (EMCs), that were prepared by ball-milling appropriate amounts of $LiBH_4$ with $Mg(BH_4)_2$, $Ca(BH_4)_2$ and $LiBH_4$ to reach the compositions listed below.

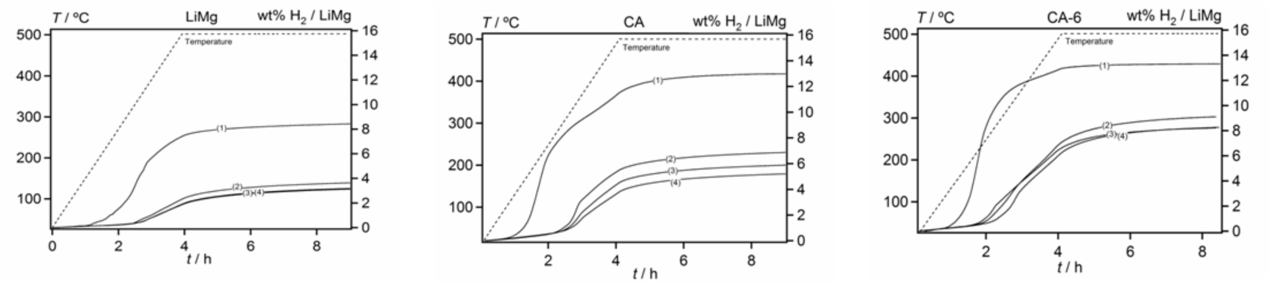
In addition, a series of different carbon hosts (microporous and mesoporous) were prepared/modified and investigated for the nanoconfinement studies. After some preliminary tests and a down-selection procedure focus was placed on the following scaffold materials:

- carbon aerogels (denoted as CA, CA-2, CA-6) with mean pore size around 30 nm, distinctively different specific surface area as well as total pore volume values,
- templated mesoporous carbons (denoted as CMK-3 and ASM) with pore size ranging from 5 to 20 nm.

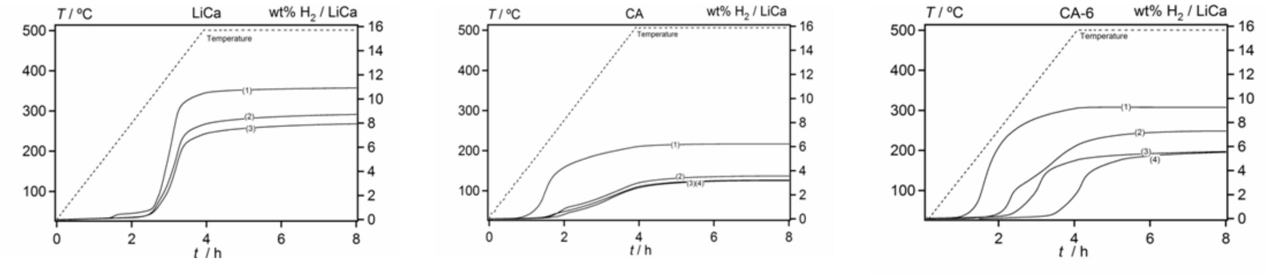
Overall it was seen that the use of carbon, either in the nanoconfined or the physically mixed samples of all types, improves notably the kinetics of hydrogen release compared to the bulk hydrides; the composites start releasing hydrogen earlier than the bulk compounds, while the main hydrogen release temperature is also shifted to (significantly in some cases) lower values, resulting in differences as high as $\triangle T_{\mathrm{onset}}$ = -130 °C (observed for the case of EMCs infiltrated in CA carbons as shown in Figure 4).

This reduction in decomposition temperature points to enhanced kinetics, and is clearly associated with the presence of the carbon surface. This effect could be further elucidated by the results obtained from the study of the composites based on CMK-3 and ASM carbons (NCSRD), bearing distinctively different pore sizes (in contrast to CA carbons having similar pore size). CMK-3 has a slightly stronger effect than ASM and this may be connected with the pore size (5.5 nm compared to 20 nm). However, simple mixing of the carbon scaffold and the boron hydrides practically leads to the same result, i.e. reduced release temperature and thus enhanced kinetics. The latter may indicate that a catalytic mechanism is perhaps prevailing whereas the confinement effect, although existing, is rather limited.

The melt infiltration of LiMg into CA carbon leads to a clear improvement of the hydrogen storage capacity, compared to the bulk material, also in terms of the reversibility of the process. This effect becomes more pronounced in the case of CA-6 carbon, which possesses the largest total pore volume and can thus accomodate larger hydride quantities. This improved stability during hydrogen release and uptake cycling was attributed to the effect of CO_2-activation, employed for the preparation of the modified CA carbons, which may lead to the formation of micropores combined with increased graphitization at prolonged activation times. The general drop in hydrogen capacity exhibited after the first desorption, indicates the formation of irreversible compound(s) residing on the scaffold. Similar observations were made for the case of the LiNa CA-based composites. In contrast, nanoconfinement did not seem to improve hydrogen storage capacity in the case of the LiCa composites which depicted inferior behaviour compared to the bulk EMC material, most likely due to the formation of stable impurity compounds upon heating.



a) LiMg



b) LiCa

Figure 5 H_2 desorption profiles of (a) LiMg and (b) LiCa bulk, nanoconfined in CA and in CA-6 during H_2 release and uptake cycling. Values of weight related capacity refer to the non-infiltrated compounds.

4.1.3.2Work package 3: Materials modelling

Objectives of the work package

The objective of this work package is to adopt quantum-chemical (QM) and CALPHAD calculations as well as kinetic modelling with an appropriate computational strategy in the simulation of boron hydrides as pure compounds and after modification with additives or with confinement. The interplay with the experimental work packages WP1 and WP2 is essential in the two directions: from computer prediction to materials synthesis and from experimental information to a subsequent modelling. Outputs of the work package were transferred to WP5, in order to estimate parameters for applications. In detail, the objectives of WP3 were:

- Modelling of structural and thermodynamic properties of pure boron hydrides
- Make computational models to interpret and predict solid state NMR data.
- Modelling the interactions between additives and pure boron hydrides
- Modelling of the effect of the confinement of boron hydrides in scaffold materials
- Modelling the thermodynamics and kinetics of hydrogen adsorption, decomposition, diffusion and chemical bonding in pure, additived and confined materials
- Matching of models with experimental thermodynamic and kinetic data (sorption properties, PXD, SANS, (A)SAXS, (E)XAFS, XANES, IR, RAMAN, NMR)

Task 3.1. Ab initio modelling of pure boron hydrides (UNITO)

(i) Phase stability and Vibrational Modes of $Mg(BH_4)_2$

For $Mg(BH_4)_2$, several inconsistencies can be found in published papers between the experimental stable phase (space group $P6_122$), denoted as α-phase, and the theoretical one. For that reason, we studied the relative stability of seven phases of $Mg(BH_4)_2$ selected among both experimentally observed and theoretically predicted polymorphs. In particular, we considered: (i) the α-phase $P6_122$; (ii) a tetragonal phase $I4_1/amd$; (iii) the β-phase, an orthorhombic phase Fddd, stable at higher temperature; (iv) the F222 phase, another orthorhombic phase which was predicted to be the most stable in many theoretical works' and (v) the $Pmc2_1$. In addition, two recently discovered polymorphs were also included: the (vi) γ– and (vii) δ–phase. The results obtained with the PBE-D* method confirm that a proper description of the dispersive forces are crucial to predict the correct order of stability, as observed experimentally and confirmed by previous calculations.

Table 1: PBE-D phase stability of $Mg(BH_4)_2$ (kJ/mol) and comparison between experimental and calculated density (g cm^{-3}).*

	ρ Expt	ρ Calc	ΔE
$P4_2nm$ (δ)	0.99	0.99	24.683
$Pmc2_1$		0.53	10.266
F222		0.56	8.928
Fddd (*β*)	0.76	0.80	8.917
Id-3a (γ)	0.55	0.57	3.823
$I4_1/amd$		1.00	0.008
$P6_122$ (α)	0.78	0.82	0.00

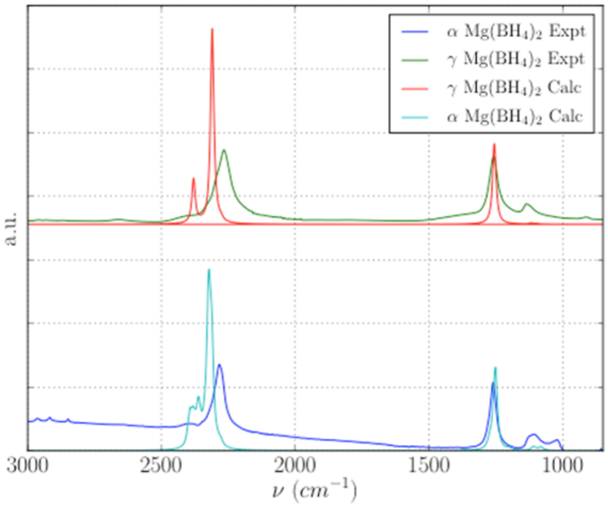


Figure 6 Experimental, represented with blue and green curves and theoretically, light blue and red curves, IR spectra of α- $Mg(BH_4)_2$ (on bottom) and γ-$Mg(BH_4)_2$ (on top). The simulated spectra were obtained with the PBED DFT functional and by using a Lorentzian function with a FWHM of 15 cm^{-1}.*

The vibrational normal modes of the two polymorphs found at room temperature (i.e. α and γ) were calculated and compared with the experimental ones. The calculated spectra, shown in Figure 6, nicely reproduce the experimental ones obtained in WP2.

(ii) Phase stability of $Ca(BH_4)_2$

For $Ca(BH_4)_2$, three phases were examined: α-$Ca(BH_4)_2$, β-$Ca(BH_4)_2$, and γ-$Ca(BH_4)_2$. The calculated crystalline structures reproduced reasonably well the experimental ones[11]. Overall, results showed an underestimation of

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[11] F. Buchter, Z. Łodziana, A. Remhof, O. Friedrichs, A. Borgschulte, Ph. Mauron, A. Zuttel, D. Sheptyakov, G. Barkhordarian, R. Bormann, K. Chlopek, M. Fichtner, M. Sørby, M. Riktor, B. Hauback, and S. Orimo, J. Phys. Chem. C 112 (2008) 8042

the unit cell size with respect to the experimental data. Calculations of the phase stability for the various phases indicate that the formation energy of the α phase is only marginally different from that of the β and γ phases, confirming that the α and β phases of $Ca(BH_4)_2$ can both be present in real samples, as often observed. The computed enthalpy differences between the different phases obtained with the PBE functional are in very good agreement with previous calculations performed with the same functional but using a planewaves / pseudo-potentials theoretical approach[12]: $\Delta H(\alpha \rightarrow \beta)$=8.23 kJ/mol and $\Delta H(\alpha \rightarrow \gamma)$=3.71 kJ/mol. But the PBE-D* method reverses the correct stability order, with the metastable γ-phase being slightly more stable than the α-phase.

(iii) Modelling the $Ca(BH_4)_2$ Surface through the Slab Model

The study of the relative stability of different surfaces is the first step to understand the effects of the additives on the decomposition reaction pathway and enthalpy of the metal boron hydrides. The computational approach we adopt to simulate a given surface is the so-called *slab model*[13]. The effect of the slab thickness on the surface structure and energy of formation has been carefully investigated. For the (001) face, the surface formation energy converges to a value of E_s = 0.32 J/m^2 for a slab model with thickness of about 14 Å, while the (101) is less stable with a E_s of 0.50 J/m^2 for a slab model with a thickness of about 17 Å. Therefore, the most stable surface appears to be the (001). For this reason, the calculations on the effects of additive on the decomposition pathway has been carried out on the (001) surface with a thickness of 14 Å.

(iv) Study of the surface of Pmc21-$Mg(BH_4)_2$

As for the previous work carried out on $Ca(BH_4)_2$ a detailed analysis of the surfaces of $Mg(BH_4)_2$ was performed in order to identify the most stable one. The analysis of low-index surfaces revealed that solely the (110), (010) and (100) faces are physically reasonable, that is stoichiometric and non-polar. It turns out that the relative stability of the different faces is: (010) > (110) > (100). The (010) face was then used as a model structure of the surface of $Mg(BH_4)_2$ in order to simulate the inclusion of additives.

An important by-product of the study of the relative stability of the different surfaces of $Pmc2_1$- $Mg(BH_4)_2$ is the possibility to model nanosizing effects on the decomposition of magnesium boron hydride. To this purpose, one can refer to the slab model as a thin film of a given thickness and consider the nanosizing process as the decomposition of films of decreasing thickness. In this study, we considered the following reaction:

$$Mg(BH_4)_2\ (s) \rightarrow MgH_2\ (s) + 2\ \alpha\text{-}B\ (s) + 3\ H_2\ (g) \qquad (1)$$

in which, along with molecular hydrogen, magnesium hydride and α-boron are formed. It can be clearly seen that the decomposition energy decreases when the thickness of the thin film reduces. This confirms that nanosizing effects can lead to a remarkable reduction of the decomposition energy when the slab thickness is below 2 nm. Not unexpectedly, nanosizing effects are more significant for the less stable surfaces with a decrease of decomposition energy between 5 and 15 kJ/mol. When considering that nanosized particles of $Mg(BH_4)_2$ can expose different surfaces at the environment, a net reduction of the decomposition energy of 10 kJ/mol can be predicted.

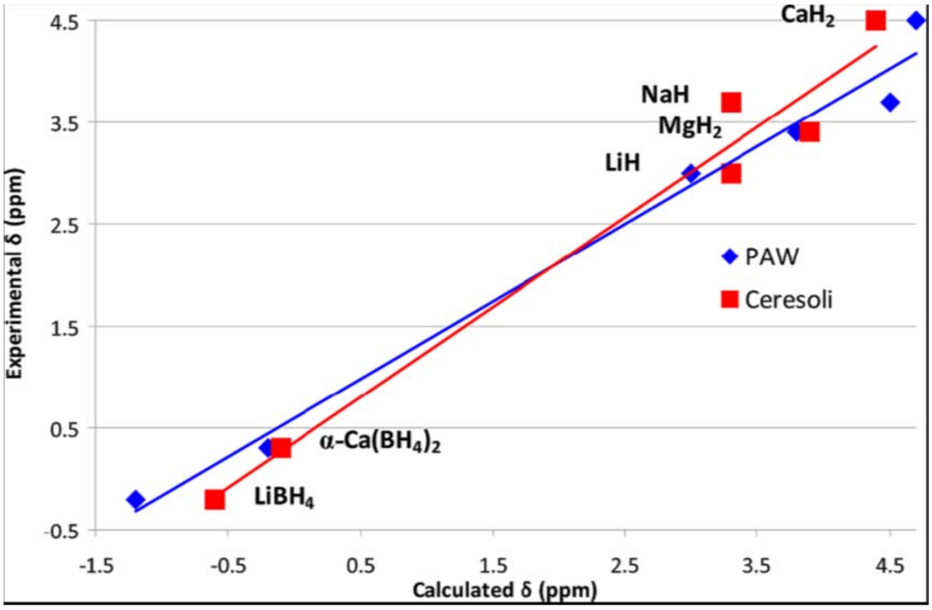

Figure 7 Experimental vs calculated 1H chemical shifts (TMS as reference).

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[12] A. Borgschulte, R. Gremaud, A. Zuttel, P. Martelli, A. Remhof, A. J. Ramirez-Cuesta, K. Refson, E. G. Bardaji, W. Lohstroh, M. Fichtner, H. Hagemann, and M. Ernst Phys Rev. B 83 (2011) 024102.

[13] R. Dovesi, B. Civalleri, R. Orlando, C. Roetti, V.R. Saunders, Rev. Comp. Chem. 21 (2005)

(v) Coupling Solid-State NMR with GIPAW ab Initio Calculations in Metal Hydrides and Boron hydrides(UNITO)[14]

An integrated experimental-theoretical approach for the solid-state NMR investigation of a series of hydrogen storage materials has been developed. Seven experimental room-temperature structures of groups I and II metal hydrides and boron hydrides, namely, NaH, LiH, $NaBH_4$, MgH_2, CaH_2, $Ca(BH_4)_2$, and $LiBH_4$, were computationally optimized. The reliability of the optimized structures was checked by comparing experimental and computed solid-state NMR parameters (such as chemical shift and quadrupolar coupling constant). A good agreement between experimental and computed multinuclear chemical shifts was obtained (c.f. Figure 7). Results of crystal geometries for low-symmetry boron hydrides ($LiBH_4$ and $Ca(BH_4)_2$) were in accordance with similar DFT based computational studies. Calculated SSNMR parameters (chemical shifts, quadrupolar coupling constants, and CSA) showed good correlation with experimental values. A maximum deviation of 1 ppm for PAW PP with respect to the experimental ^1H SSNMR chemical shifts was found. In summary, we were able to validate a new set of PAW PP showing that the predicted SSNMR ^1H, ^{23}Na, and ^6Li chemical shift values obtained by using PAW PP are analogous to those derived by employing the standard QE PP. In addition to this, a substantial improvement of the ^{11}B chemical shift estimation was obtained adopting PAW PP.

Task 3.2 Ab initio modelling of the role of additives (UNITO)

(i) Additive effects: Co, Ni, Cu and Zn at the $Ca(BH_4)_2$ surface

On the basis of the studies performed in Task 3.1, we simulated the insertion of additives on top of a $Ca(BH_4)_2$ (001) surface. The Ni^{2+} ion was selected as additive. The inclusion of the Ni ions in the pure boron surface appears to destabilize the anion by inducing a distortion of the BH bonds linked to the transition metal, which in turn implies an easier decomposition mechanics. We then extended our simulation by investigating the insertion of four different additives (i.e. Co, Ni, Cu, Zn) on top of the $Ca(BH_4)_2$ (001) surface which was predicted to be the most stable one. Results showed that the presence of the additive in the structure leads to a remarkable re-arrangement of the top most layer and in particular of its first coordination sphere. The closest $[BH_4]^-$ ion, indeed, appears very distorted with respect to the pure system. By a close inspection of the effect of the additive in the deformation of the $[BH_4]^-$ group, it is clear that it decreases on going from Co^{2+} to Zn^{2+}. The Co^{2+} and Ni^{2+} ions appear to be the most effective ones. In those two cases, indeed, the two B—H bonds pointing towards the cation appear elongated by more than 7% with respect to Ca^{2+}, and the angle between these two bonds is decreased by 5.6%.

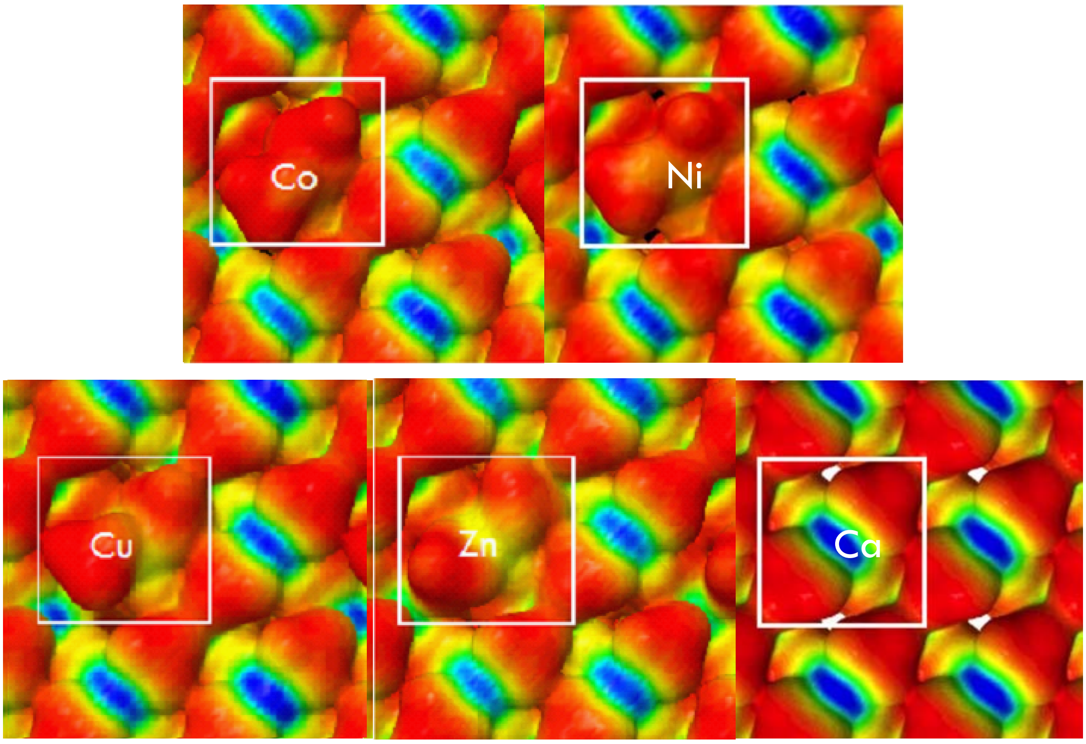

Figure 8: Top view of electrostatic potential (min: -0.029 a.u. (red); max: +0.246 a.u. (blue)) mapped on top of the charge density isosurface (i.e. 0.003 a.u.) for all the optimized structure. The region of interest is highlighted by the white box.

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[14] Federico Franco, Marcello Baricco, Michele R. Chierotti, Roberto Gobetto, Carlo Nervi, *J. Phys. Chem. C*, **2013**, *117* (19), 9991–9998.(**DOI:** 10.1021/jp3126895)

When moving from Co^{2+} to Zn^{2+}, the general trend observed for the structural features of the nearby boron hydride anions is confirmed, in spite of the very similar electronegativity for Co, Ni, Cu and Zn. The BH^0_4 ”anion” is thus unstable. The less ”anionic” character of the $[BH_4]^-$ group is highlighted by the Mulliken atomic charges of the two cations and of the adjacent $[BH_4]^-$ anions. A decrease up to 72% is observed, confirming that a more electronegative cation (Pauling electronegativity from 1.0 to 1.8, for Ca and Ni, respectively) involves a lower charge transfer. By comparing the four cations, Ni^{2+} and Co^{2+} appear to have a greater influence on the $[BH_4]^-$ charge distribution. For these two metals, the $[BH_4]^-$ predicted charge is about -0.3, with a remarkable decrease of 60% with respect to Ca^{2+}; whereas for Cu^{2+} and Zn^{2+}, the charge is -0.5, with a decrease of about 30%.

(ii) Ni-based additives and CuF_2 on the $Mg(BH_4)_2$ surface

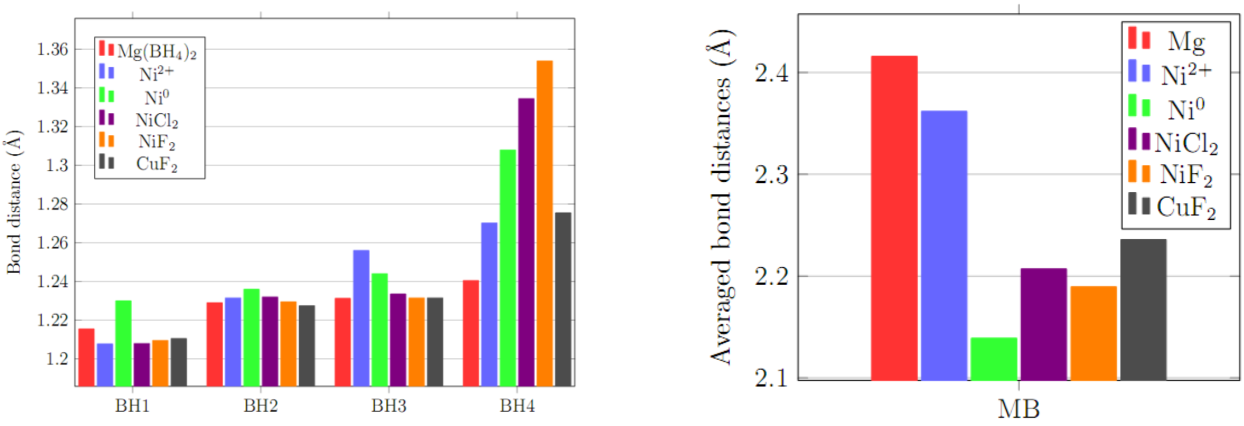

Figure 9: Average B-H bond distances (Left) and average M-B bond distances (Right) for the nearest neighboring $[BH_4]^-$ groups of the metal.

On the basis of previous results as reported in Task 3.1, we simulated the insertion of various Ni-based species on top of the *Pmc2₁*- $Mg(BH_4)_2$ (010) surface. In particular, three different kinds of additive species were explored, namely: Ni^{2+} as a substitutional defect; atomic Ni^0 as an interstitial defect and a doping with nickel halides (i.e. NiF_2 and $NiCl_2$). Along with NiF_2, we also modelled the insertion of CuF_2 at the surface.

As already observed for additives on the $Ca(BH_4)_2$ surface, the presence of the additive in the structure leads to a remarkable re-arrangement of its first coordination sphere. The closest $[BH_4]^-$ ion, indeed, appears very distorted with respect to the pure system. The deformation of the B-H bond lengths is then considered as an indicator of the propensity of the boron hydride to decompose: the larger the deformation (i.e. the longer the bond distance) the weaker the bond and the easier the decomposition.

The average structural deformation of the $[BH_4]^-$ groups around the metal can be clearly seen from Figure 9 (left). For all additive species, an elongation of the B-H bonds is observed with respect to the undoped surface (see Figure 9). The effect of the metal on the B-H bond distance is particularly relevant for both NiF_2 and $NiCl_2$ substitutions. Interestingly, CuF_2 is not as effective as Ni-based additives in perturbing the $[BH_4]^-$ anions. Therefore, it is expected that Ni would outperform Cu in favouring the decomposition of magnesium boron hydride.

In addition, it is important to point out that also the Ni-B distance can be used as a further indicator of the increased propensity toward dissociation of the boron hydride. In fact, IFE have shown that the decomposition of $Mg(BH_4)_2$ in presence of Ni-based additives occurs always through the formation of the metal boride. Therefore, a shorter Ni-B distance can be interpreted as an increased tendency to the decomposition of the $[BH_4]^-$ groups. As shown in Figure 9 (right), Ni^0 in the interstitial site leads to a remarkable shortening of the mean Ni-B distance in the doped $Mg(BH_4)_2$ followed by Ni and Cu halides. Overall, computed results indicate that NiF_2 is the most effective additive among the investigated ones.

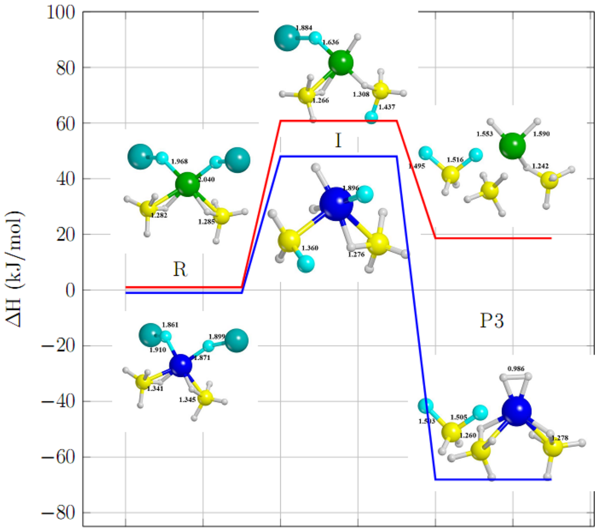

Figure 10 Comparison of the decomposition pathway to doubly substituted F-boron hydride for NiF_2 and CuF_2 based additives. For both additives, the zero of the reaction enthalpy has been referred to the reagents.

Reactivity of NiF_2 and CuF_2 on the $Mg(BH_4)_2$ surface

Stimulated by previous results, we extensively investigated the reactivity of NiF_2 at the *Pmc2₁*-$Mg(BH_4)_2$ (010) surface. Some results were also obtained for CuF_2. In Figure 10, the enthalpy of reaction for the pathway from reagent (R) to product P3 is graphically reported. While the formation of the intermediate (I) is endothermic the reaction to product P3 is favoured because of the stability of the chemisorbed hydrogen atoms, as already mentioned, but also because of the combination of the stabilization of the $[BH_2F_2]^-$ group and the attractive ionic interactions between F and Mg.

On the basis of the latter results on NiF_2, the same reaction pathway was explored for CuF_2. Although the Cu-based intermediate is similar to the Ni-containing one, the product, a doubly substituted F-boron hydride, shows a significantly different geometry with well-separated hydrogen atoms on the chemisorbed CuH_2. Furthermore, the overall reaction enthalpy is endothermic. As the stabilizing effects discussed above are also present in this case, this result demonstrates the better capacity of Ni to chemisorb hydrogen than Cu.

(ii) Nano-Confinement: $Ca(BH_4)_2$ cluster on graphene surface

The interaction of the selected pure $Ca(BH_4)_2$ with carbon-based scaffold models have been simulated to better understand the chemical bonding and to shed some light on the decomposition mechanisms.

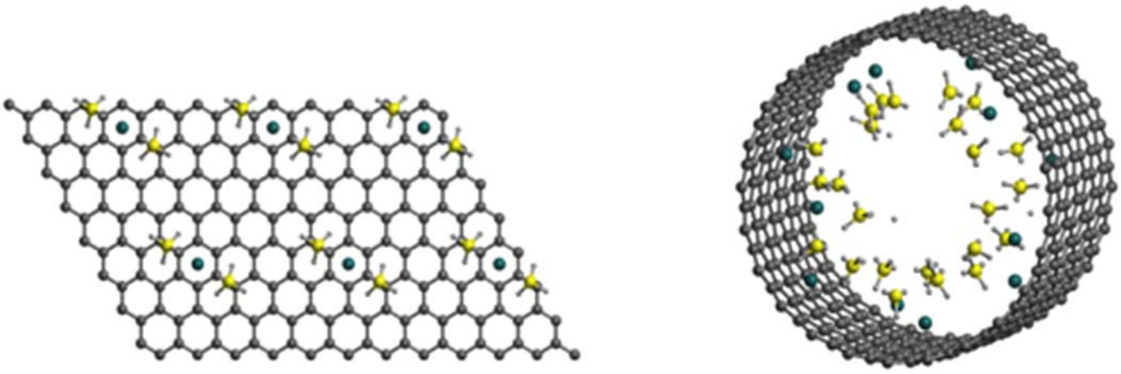

Figure 11 Two model systems of nanoconfinement: Ca(BH4)2 unit formula on the graphene (left) and inside the nanotube (right). C is grey, Mg green, B yellow and H white.

To estimate the effect of the nanoconfinement on the B—H bonds and then on the decomposition enthalpy of the boron hydride, the energy of interaction E_{int} and the deformation of the cluster have been analysed. The computed value reveals a weak interaction energy of $E_{int} = 11.1$ kJ/mol. The size of the $Ca(BH_4)_2$ cluster has then been increased from 1 to 2 formula units (2-FU). The full optimization of the structure (i.e. both atomic positions and cell parameters) leads to the formation of an unexpected chain-type structure of $Ca(BH_4)_2$ with all the atoms being spread over the entire surface. Future refinements of the nanoconfined $Ca(BH_4)_2$ model, as the building of a larger 2D graphene supercell or a more spherical cluster, may shed some light on this behaviour.

To estimate the effect of the carbonaceous support on the atomic distances, a comparison among the relevant structural features of the naked $Ca(BH_4)_2$ molecule, the 1-FU and 2-FU cluster models has been carried out. The cluster-support interaction does not appear to be strong enough to influence significantly the B—H bond (percentage difference of -0.24 for the 1-FU and -0.56 for the 2-FU with respect to the free $Ca(BH_4)_2$ molecule) and then the decomposition enthalpy. The improvement of the decomposition process observed for boron hydrides nano-confined in carbon scaffolds could be then due to the catalytic and the size effects induced by the nano-confinement.

Task 3.3. Thermodynamic and kinetic modelling (HZG, IFE, AU, UNITO, Empa)

(i) Thermodynamic modelling of $Mg(BH_4)_2$ (UNITO)

To our knowledge, a real assessment according to the CALPHAD approach[15] and based on the comparison of several thermodynamic data, is not available for $Mg(BH_4)_2$. Therefore, the first part of the work was aimed to the assessment of the Gibbs Free Energy (GFE) function for alpha, beta and gamma polymorphs of $Mg(BH_4)_2$. The description of thermodynamics and kinetics of hydrogen desorption from β-$Mg(BH_4)_2$, to be compared with experimental results obtained in WP2, was carried out on a model system because of the big size of unit cell of β -$Mg(BH_4)_2$ (more 320 atoms). The selected model system was the theoretically predicted *Pmc2₁* phase (22 atoms in the unit cell). The hypothesis we made on the basis of the relative stability and density is that the two phases could show a similar behaviour toward decomposition. Then, using our new functions for $Mg(BH_4)_2$

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[15] H L Lukas, S G Fries and B Sundman, Computational Thermodynamics, the Calphad Method, Cambridge University Press (2007)

together with that for the other compound already reported in thermodynamic databases,[16] phase diagrams have been calculated. Despite thermodynamic data about $Mg(BH_4)_2$ are scattered, a fairly good agreement between PCI data and *ab initio* calculations can be observed. Concerning calorimetric measurements, instead, an underestimation of the stability of this compound has been evidenced.

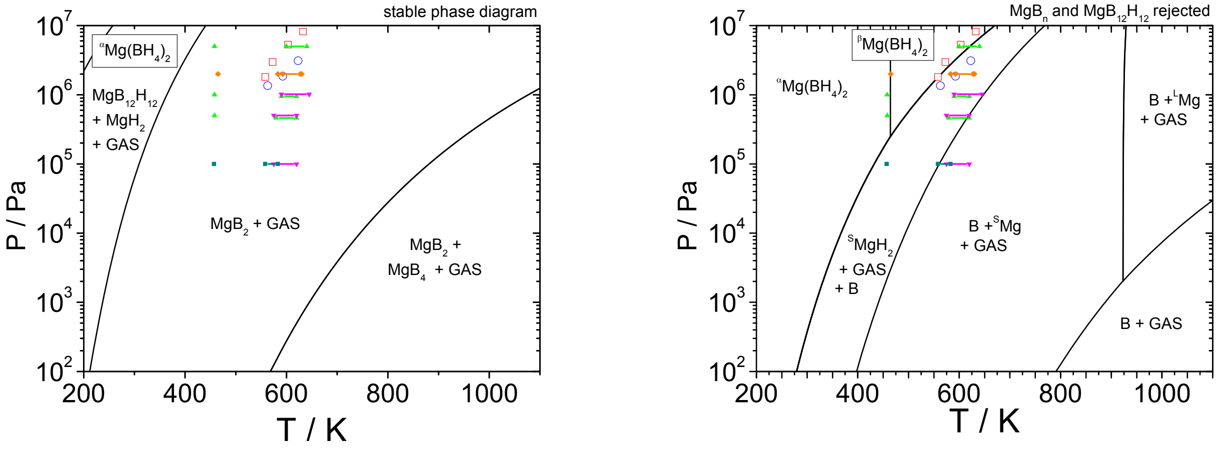

Figure 12 Calculated phase diagrams for $Mg(BH_4)_2$ composition. Stable phase diagram obtained considering all phases is shown on the left. Metastable phase diagram obtained rejecting $MgB_{12}H_{12}$ and magnesium borides is shown on the right. PCI and DSC data from literature are reported for comparison.

Using Gibbs Free energy functions, based on experimental data and *ab initio* calculations, together with those reported in the Substance database,[16] stable and metastable phase diagrams for $Mg(BH_4)_2$ composition were calculated and results are shown in Figure 12. Furthermore, driving forces for different dehydrogenation reactions have been calculated and are reported in Figure 13.

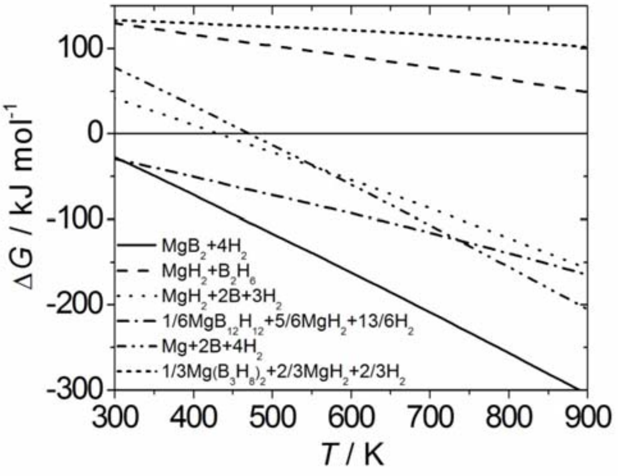

Figure 13 Calculated driving forces for the dehydrogenation of $Mg(BH_4)_2$ into different products for P_{H2}=1bar.

Thermodynamic modelling of $Ca(BH_4)_2$ (UNITO)

The same approach that was used for $Mg(BH_4)_2$ was adopted to describe the thermodynamics of $Ca(BH_4)_2$.

The calculated temperature versus pressure stable phase diagram is reported in Figure 14. A good agreement between experimental and theoretical data is observed for the polymorphic trasformation and for the dehydrogenation raction even if for lower pressures (and therefore lower T) experimental points are slightly shifted to higher temperatures. The driving forces for reactions leading to the formation of different products for P=1 bar are reported in Figure 15.

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[16] SGTE Substance database v4.1

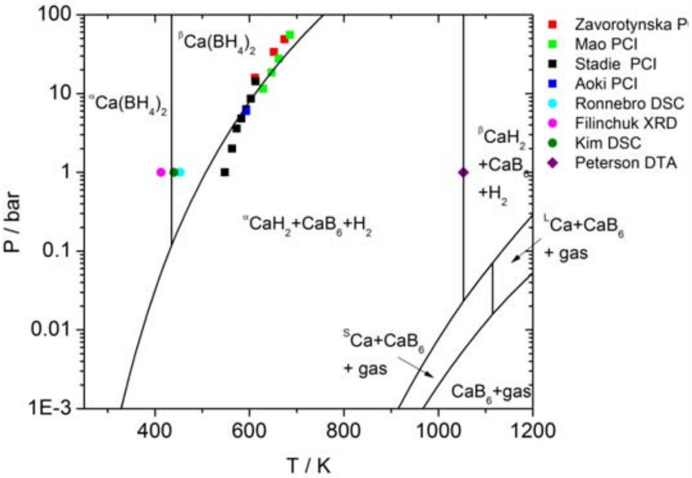

Figure 14: Stable phase diagram calculated for $Ca(BH_4)_2$ composition. Experimental data from project partners and from the literature are reported for comparison.

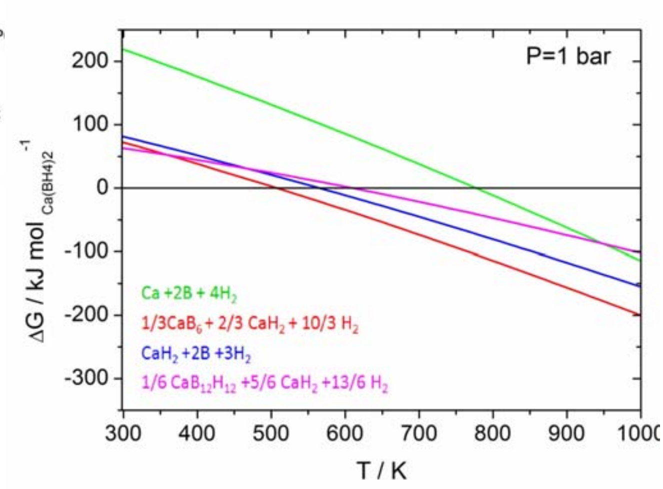

Figure 15: Calculated driving forces for the dehydrogenation of $Ca(BH_4)_2$ into different products for P_{H2}=1bar.

(ii) Thermodynamic description of the 2LiBH4+MgH2 system (HZG, UNITO)

In order to be able to calculate reaction heats and optimise the design of the prototype hydrogen storage tank, which should operate with this Li-RHC as the storage material, the thermodynamic parameters of the expected reactions were determined. A single step decomposition process is expected for this system, according to the reaction:

$$2\ LiBH_4 + MgH_2 \rightarrow MgB_2 + 2\ LiH + 4H_2 \qquad (1)$$

and the dehydrogenation temperature of the mixture is predicted to be lower than that of both pure $LiBH_4$ and pure MgH_2. However, experimental investigations[17] show that a two-step dehydrogenation reaction,

$$2LiBH_4+MgH_2 \rightarrow Mg+2LiBH_4+H_2 \rightarrow MgB_2+2LiH+4H_2 \qquad (2)$$

occurs, suggesting that full equilibrium conditions are not reached and that the formation of MgB_2 is hindered until Mg is produced by the dehydrogenation of MgH_2.

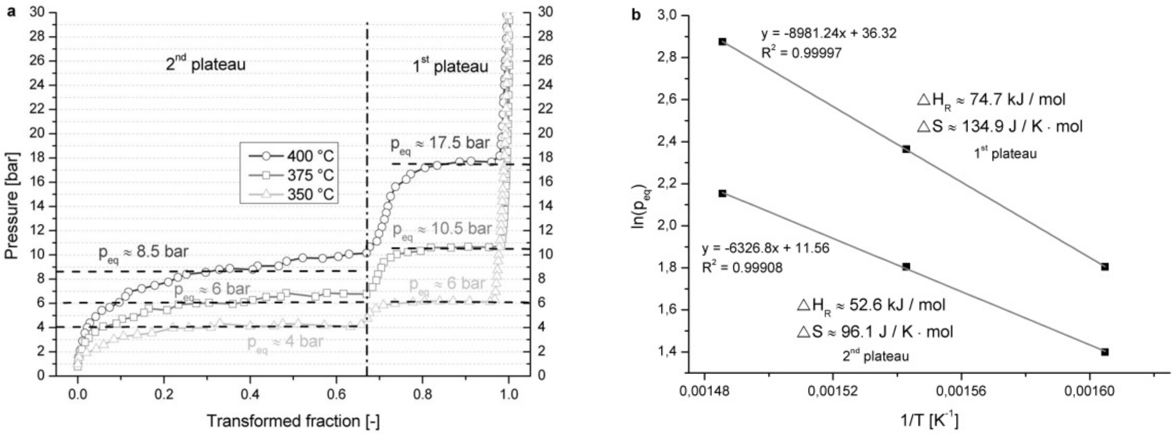

Figure 16 (A) Pressure concentration isotherms under desorption conditions at 400 °C, 375 °C and 350 °C
(B) van’t Hoff plot for first and second plateau

A reaction enthalpy value of 74.7 kJ mol_{H2}^{-1} and entropy value of 134.9 J mol_{H2}^{-1} K^{-1} have been calculated for the first plateau. According to the Van’t Hoff plot of the second plateau, an enthalpy of 52.6 kJ mol_{H2}^{-1} and entropy of 96.1 J mol_{H2}^{-1} K^{-1} have been determined (Figure 16). The corresponding equilibrium pressures for the calculation are also indicated in Figure 16A (dashed lines). The first value corresponds with assessed value of dehydrogenation of MgH_2, as described in the first step of eq. 2, whereas the second value needs further investigations. A more direct measurement of the enthalpy of reaction can be performed coupling the Sieverts apparatus with the HP-DSC. An enthalpy value of -32.3 kJ mol_{H2}^{-1} was obtained, in reasonable agreement with

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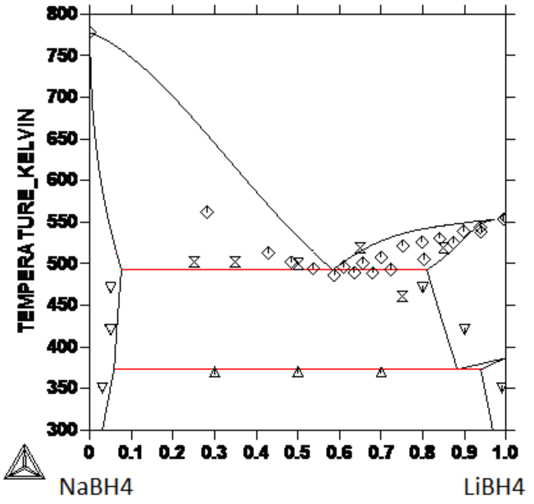
[17] U. Bosenberg, S Doppiu, L. Mosegaard et al. Acta Materialia 2007;55, 3951

values reported in the literature[17]. Moreover the specific heat capacity of the composite $LiBH_4$+MgH_2 was calculated to be 1.30 kJ / (kg * K) and it is clearly dominated by the heat capacity of MgB_2.

(iii) Thermodynamic modelling of eutectic mixtures of boron hydrides

Following the experimental activity carried out by the University of Aarhus in the framework of WP2, a thermodynamic description of eutectic boron hydrides mixtures has been explored. The three binary systems $LiBH_4$-$NaBH_4$, $NaBH_4$-KBH_4 and KBH_4-$LiBH_4$ have been modelled. For the $NaBH_4$ - $LiBH_4$ system, the interaction parameter Ω = -11 kJ mol^{-1} for the liquid phase confirms the stability of the liquid mixture with respect to the cubic and orthorhombic cubic solid solutions. In the case of the $NaBH_4$ - KBH_4 system, the introduction of a positive interaction parameter for the cubic solid solution $^{CUB}\Omega$ = 9 kJ mol^{-1} was able to reproduce fairly well the behaviour of the miscibility gap. Considering this positive interaction parameter, an ideal behaviour for the liquid phase is hence enough to stabilize the liquid mixture with respect to the solid solution and reproduce experimental points for the liquidus and solidus lines. The phase diagram for the KBH_4-$LiBH_4$ system (Figure 18) shows a regular liquid solution. The strongly negative interaction parameter $^{LIQ}\Omega$ = -14 kJ mol^{-1} is consistent with the deep eutectic obtained for this binary system.



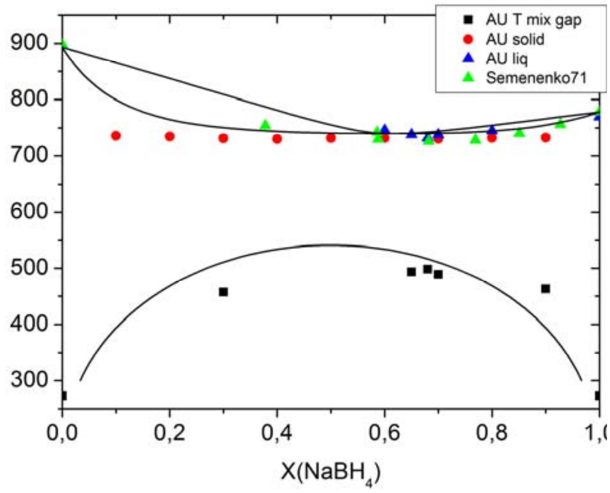
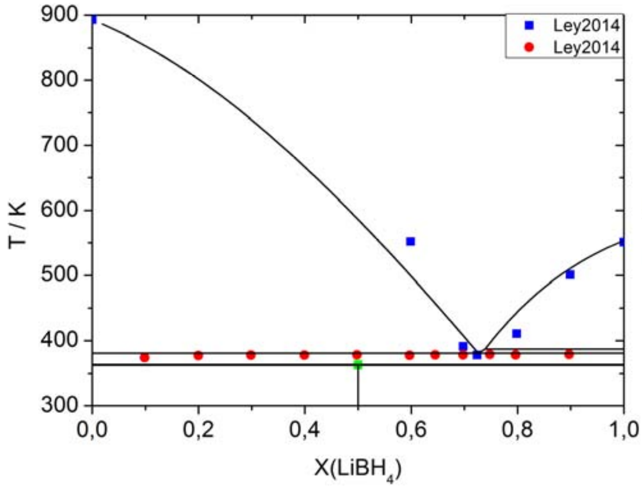


Figure 18: Calculated phase diagram for $NaBH_4$ - $LiBH_4$ system for P_{H2}=1bar considering solubility (lines). Experimental points obtained from literature and from AU experiments.

Figure 17: Calculated phase diagram for $NaBH_4$ - $LiBH_4$ system for P_{H2}=1bar (lines). Experimental points obtained form the literature and from AU experiments.



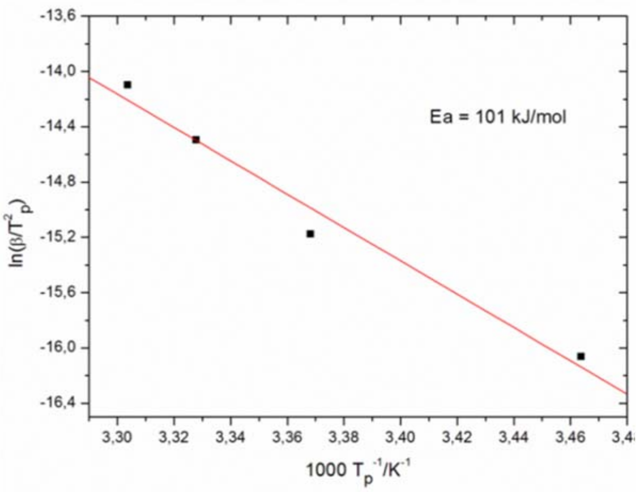


Figure 18: Calculated phase diagram for KBH_4 - $LiBH_4$ system for P_{H2}=1bar (lines). Experimental points obtained from the literature and from AU experiments.

Figure 19: Kissinger plot constructed for γ-$Mg(BH_4)_2$ decomposing under Ar flow at various temperature rates (2K, 5K, 10K, 15K). Peak temperatures (288 - 302°C), obtained from DSC data, have been used.

(iii) Kinetic modelling of $Mg(BH_4)_2$ (AU)

AU has constructed a Kissinger plot for determining the apparent activation energy for decomposition of γ-$Mg(BH_4)_2$ (Figure 19). Based on the slope of the graph, an extracted value of apparent activation energy amounts to approximately 101 kJ/mol.

4.1.3.3Work package 4: Cost effective materials synthesis

Objectives of the work package

It was the objective of this work package to develop and study routes suitable for industrial scale production of the storage materials selected in WP1 and WP2 with special regard to

- developing a competitive production technology based on wet chemical synthesis, or high energy milling under protective or reactive atmosphere, or combinations of these techniques,
- processing of cost effective raw materials, being available in large quantities at reasonable prices with high security of supply,
- assessing the effect of degree of purity of the storage materials on hydrogen sorption properties and cycling stability in conjunction with potential cost reductions, and
- establishing the necessary environment of a prototype production route with respect to reliability and reproducibility of materials production, as well as safety issues connected to processing of boron based materials, additives and flammability and hazardousness of powders containing light metals and boron.

In order to achieve these objectives, which are tightly connected with the kind of hydrogen storage material to be synthesised, WP4 centrally for BOR4STORE took over the task of rigorously supervising the downselection process on possible combinations of storage materials (⇒ WP1, WP4), additives (⇒ WP2) and scaffold materials (⇒ WP2) and connected routes for materials synthesis (⇒ WP1, WP4).

Task 4.1 Materials evaluation and downselection for tank testing (HZG, BOR4STORE General Assembly)

The following criteria were reviewed for each investigated material and applied for materials downselection:

- capacity of > 80 kg H_2/m^3. As the materials to be investigated have densities around 0.5 to 1.5 g/cm^3, this translates to weight related capacities of > 5 wt.% to > 16 wt.%
- reaction enthalpy <50 kJ/(mol H_2),
- material releases H_2 for $T \leq 450$ °C
- potential for materials cost below 500 € / kg of stored H_2 in the long term
- H_2 absorption to full capacity in 1 hour or less
- material at least 90% reversible

As material selected for testing in prototype tank, the materials downselection process, yielded as the most promising boron hydride material the compound $LiBH_4$ – MgH_2 (in its hydrogenated form) and LiH-MgB_2 (dehydrogenated form), denoted as Lithium based Reactive Hydride Composite Li-RHC. Features are:

- hydrogen storage capacity theoretically 11.5 wt.%, experimentally including additive ca. 8.5 – 10 wt.%
- materials density, depending on degree of compaction of the powder between 0.6 and 1.5 g/cm^3, yielding ca. 50 – 150 g H_2/l on materials level.
- temperature of hydrogenation for acceptable reaction speed below 1 h ca. 350°C.
- hydrogenation possible at 30 bar. Preferred hydrogenation pressure ca. 50 bar. Still faster kinetics can be obtained by increasing the hydrogenation pressure.
- dehydrogenation temperature at 5 bar hydrogen pressure ca. 400 - 450°C for suitable reaction speeds
- materials cost for BOR4STORE ca. 7,000 €/kg of stored hydrogen, currently minimum cost, if it could be purchased in tonnage quantities and based on raw materials cost, ca. 3,500 €/kg of stored hydrogen

Further most interesting materials were

- $Mg(BH_4)_2$: theoretically 15 wt.%, practically so far a few wt.% reversible capacity at T < 280°C
- Carbon aerogel scaffolds, infiltrated with a $LiBH_4$-$Ca(BH_4)_2$ eutectically melting composite. The infiltrated material achieved a reversible capacity of ca. 60% after 3 cycles, which amounted, due to the inert scaffold material, to ca. 4 wt.% of absolute hydrogen storage capacity

Task 4.2 Evaluation of potential sources for cost effective raw materials (HZG, ZOZ, KAT, AU, NCSRD)

(i) Sources and suppliers for pure boron hydrides (KAT)

Commercially available boron hydrides ($NaBH_4$, $LiBH_4$) today can be obtained from fine chemical suppliers (Alpha Aesar, Sigma Aldrich) in small amounts up to the kg scale. Alternative and more cost effective suppliers can be found in Russia and China, but the quality of these compounds might vary. Analysis of Katchem showed, that $LiBH_4$ can be obtained at ca. 120 - 700 €/kg (Chinese and Russian suppliers) in the kg scale today. No production at larger scale is available for this compound, whereas $NaBH_4$ can be obtained at cost as low as 25 €/kg, since it is widely used in the chemical industry as a reducing agent, and can be rather readily synthesized from natural ores of borax (sodium boron oxide). The much higher cost of $LiBH_4$ and correspondingly $Ca(BH_4)_2$ and $Mg(BH_4)_2$ is due to the following wet chemical route for conversion of $NaBH_4$ and especially necessary purification steps after the metathesis reaction of $NaBH_4$ with LiCl, $CaCl_2$ and $MgCl_2$, respectively.

Cost analysis of a wet chemical route starting from borane complexes as Boron source yielded no cost advantage, according to Katchem's analysis. The method developed at AU for synthesis of boron hydride materials (patent applied for) holds the potential to be almost indifferent towards purity of raw materials due to an optional intrinsic purification step combined with the synthesis itself (for $LiBH_4$). Thus, the products purity will not necessarily be affected by the purity of starting materials in this specific case.

(ii) Sources and suppliers for raw materials synthesis of Reactive Hydride Composites (ZOZ)

Focusing on 4 different routes for synthesis of the Li-RHC ($LiBH_4$-MgH_2), Zoz did a market analysis of suppliers of different educt compounds to be used in the synthesis. Concluding, it can be said

- $LiBH_4$ can be obtained at several hundred Euros per kg, in tonnage quantities there might be the potential for < 200 €/kg
- The most cost effective route for synthesis of boron hydrides is to synthesise the dehydrided compounds and then hydrogenate them *in situ*, e.g. in the hydrogen storage tank.This applies e.g. to the Li-RHC, where the most cost effective route is to synthesise the LiH-MgB_2 mixture.
- Other, more rare or industrially not available boron hydride compounds easily reach cost of several thousand to significantly more than 10,000 Euros/kg, preventing from being useful for hydrogen storage.
- Novel, completely dry routes for synthesis of boron hydride based compounds, starting from the ores (e.g. boron oxide and Na, Li or their hydrides) remain to be investigated, but it looks like being difficult to achieve a target of lower than 50 €/kg, necessary for obtaining a cost of 500 €/kg of stored hydrogen at 10wt.% hydrogen storage capacity.

Task 4.3. Effects of use of cost effective raw materials on materials properties (HZG, ZOZ, KAT, AU)

HZG could demonstrate, that it is possible to synthesise storage materials, using an Mg alloy from scrap (Figure 20).

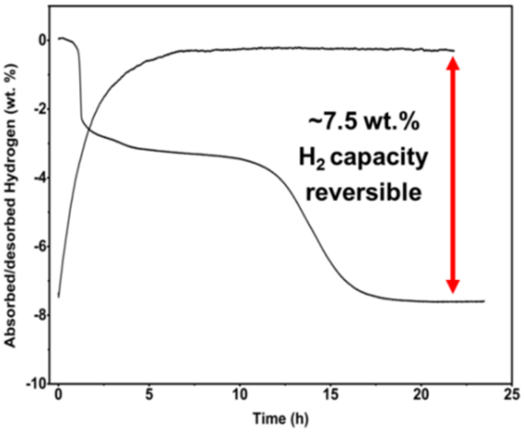


Figure 20: A Li-RHC from a $LiBH_4$ with 95% purity and a waste Mg-Gd alloy shows a reversible hydrogen capacity of 7.5 wt.%. desorption at 3 bar H_2, 400°C; absorption at 50 bar H_2, 350°C.

In order to further reduce materials cost, the effect of the purity of $LiBH_4$ on the system sorption properties was investigated. Lower purity material is expected to be ca. 10 – 20% cheaper than high purity material. For this reason two batches of TiCl3 doped $LiBH_4$ + MgH_2 were prepared using $LiBH_4$ with a purity of 85 and 95%. For the material synthesized with the high purity $LiBH_4$, the hydrogenation cycles show a more marked decrement of the total hydrogen capacity than with the low purity $LiBH_4$ (Figure 21). This difference in degradation rate is most likely connected with a more marked phase separation in the system prepared with $LiBH_4$ 95 % purity. For this system besides the decrement of the hydrogen capacity it is possible to observe also a marked slowing down of the absorption kinetics. In conclusion, the use of lower purity $LiBH_4$ for hydrogen storage purposes appears promising both from the point of view of reducing the cost of the storage material and from the point of view of the hydrogenation/dehydrogenation performances.

Task 4.4. Safety issues (HZG, ZOZ, KAT, AU)

(i) Laboratory scale handling and safety

A categorization of most borohydride materials as being ***air-sensitive*** (except $NaBH_4$ which can be handled freely) is suitable. All laboratory-scale handling of materials has to be carried out in gloveboxes (O_2/H_2O < 0.5 ppm). For wet chemical processing, Schlenk techniques (i.e. drying and evacuating/filling glass vessels / containers / equipment w. inert gases), whereas all laboratory type high energy mills are placed inside glove

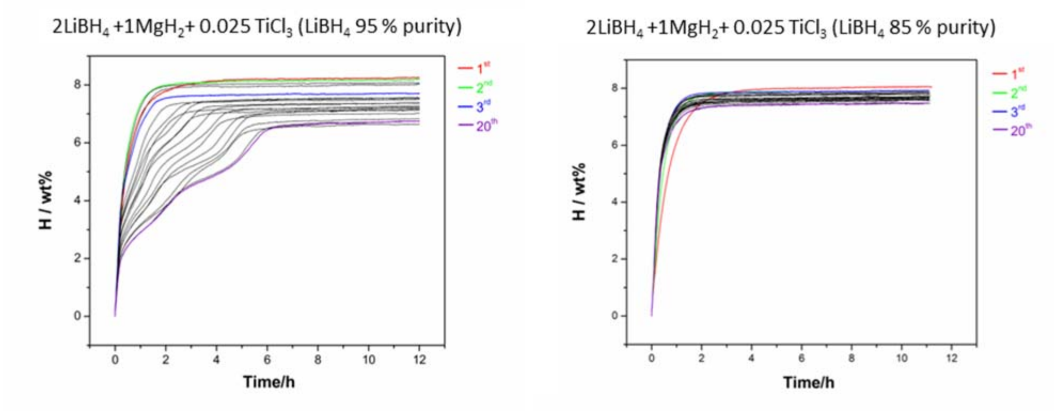


Figure 21: Absorption cycles $2LiBH_4 + 1MgH_2 + 0.025\ TiCl_3$ with $LiBH_4$ 85 % purity (right side) and with $LiBH_4$ 95 % purity (left side)

boxes. Furthermore, certain materials are to be stored below RT, not necessarily due to *safety* issues, but rather due to instability of e.g. a specific polymorph of the material.

For waste disposal of the usually flammable and often self-ignitable compounds, usually a controlled and slow oxidation process in special bins, but with normal atmosphere is employed. This leads to inert compounds, which easily can be disposed or burnt as normal chemical waste by specialised companies.

(ii) Processing of hydrogen storage materials on industrial scale in ZOZ Simoloyer®

In contrast to the usually used processing of small amounts of materials in the less than 100 g range (mostly less than 5 – 10 g) under inert atmosphere in glove boxes, the ZOZ Simoloyer® High Energy Ball Mill, used in BOR4STORE for scale-up of materials processing, can only be operated with internal inert atmosphere. I. e. all parts of the processing device from the educt materials container over the charging tubes for the grinding unit, the chamber itself, and also the uploading tubes towards the product container are flushed with e.g. Argon, but no external inert atmosphere is needed which allows for the High Energy Ball mill with all its attachments operating in normal ambient atmosphere. It was shown by ZOZ and HZG, when doing the materials processing for the storage material to be filled into the hydrogen tank, that this type of mill is suitable for processing of also oxygen and humidity sensitive materials like the Li-RHC. With this type of mill, processing cost below 1 €/kg of processed materials on larger scale seem to be feasible, i.e. being negligible compared to the materials cost.

Task 4.5 Routes for cost effective materials synthesis (HZG, ZOZ, KAT, AU

(i) Cost analysis of wet chemical production route for synthesis of pure boron hydrides (KAT, AU)

AU analysed different routes for wet chemical synthesis of boron hydrides and generally found, that it was significantly cheaper (factor 10 or higher) to synthesise boron hydrides starting from metal hydrides and sodium boron hydride or sodium boron hydride and metal clorides than buying the final boron hydride from commercial suppliers. Conclusively, the materials produced at AU are cheaper than commercial sources, but do not take into account *provision*, *equipment*, *labour*, *facilities-rent/maintenance* etc. The survey shows that there are large differences in the price ranges available from commercial sources to non-commercial sources. I.e. prices vary strongly in terms that cannot be ascribed to different costs of raw materials, rather different market-strategies for different companies might be the actual cause.

One indicative result on potentials for cost decreases is, that currently at Katchem $LiBH_4$ is sold at ca. 700 – 1000 €/kg, whereas a Chinese supplier claimed cost of just 120 €/kg, when purchasing tonnage quantities. So a factor of 6 – 10 in cost decrease does not seem to be unrealistic when increasing the amounts of purchased materials from lab to industrial scale. Another indication is, that the theoretical cost of $Mg(BH_4)_2$ prepared in 1kg quantity in one batch by AU method is around 3.500 € per kg, whereas current prices from other commercial suppliers (c. f. Deliverable 4.8., Table 3) are around 140.000 €/kg.

(ii) Cost analysis of the route of synthesis for Li-RHC for BOR4STORE hydrogen store (HZG, ZOZ)

For synthesis of the Li-RHC, a complete dry milling process on the ZOZ Simoloyer® milling type was developed, which includes high energy processing under inert atmosphere, being confined to the internal of the milling machinery. So, no glove boxes around the mills are necessary any more. In an analysis of this milling process on larger mills, ZOZ calculated the cost for processing, based on the following factors:

- Depreciation of investment cost, maintenance of machinery,
- cost for labor, energy, water, at a processing time of 4h per batch,
- production hours: 4800 h/year with 20 years run-time of the mill

- all including a safety factor of 1.5

It could be concluded, that the cost for high energy processing alone of metal hydrides is negligible (< 2 €/kg), compared to raw materials cost and cost of further wet chemical processing steps, which might be necessary for production of raw materials and further processing after high energy milling. Therefore, in future process developments, there should be a strong focus on avoiding wet chemical processing and further purification steps as far as possible.

(iii) Cost driver analysis of synthesis and production of boron hydride based hydrogen storage materials (HZG, ZOZ, KAT)

In this joint effort, the companies of Zoz and Katchem, together with HZG performed a further cost driver analysis of solid state hydrogen storage. They found, that the main cost driver is the cost for educt materials for synthesizing the hydrogen storage compounds (cf. preceding analysis of wet chemical production and dry high energy processing). Especially the source of boron is a critical cost factor. In wet chemical routes for synthesis, costs are furthermore determined by processing times for the chemical reactions themselves and for necessary purification steps after synthesis. In mechano-chemical synthesis (high energy ball milling), materials processing times are so short (ca. 1-2 hours), that processing cost are neglible compared to educt materials cost. In the routes interesting for BOR4STORE no further purification is necessary after mechano-chemical processing. The cost of the tank hull itself in series production at low temperatures of operation than the 650°C of the BOR4STORE prototype tank would contribute only to a minor amount to the storage system cost, and cost will be dominated by that of the storage materials. World wide supplier analysis including China and Russia yielded, that at current industrial status of materials synthesis, today solid state hydrogen storage can be realized at cost of ca. 3500 – 8000 Euro / kg of stored hydrogen. Cost for the storage materials might be lowered to ca. 1,500 €/kg of stored hydrogen with respect to raw materials cost, if a large scale production at current materials prices would be set up. Cost for series production of complete solid state hydrogen tanks cannot be estimated seriously, but for sure will several 1000 Euro/kg of stored hydrogen, to be compared with the target of ca. 500 €/kg H_2 for series production of compressed hydrogen stores for light vehicles, and probably more than 1000 €/kg H_2 for liquid hydrogen stores.

Task 4.6: Techno-economical evaluation of materials synthesis and properties (ZOZ, KAT)

In BOR4STORE mainly four routes for synthesis of boron hydride compounds were used:

1. Starting from $NaBH_4$ or e.g. $LiBH_4$ as starting material and synthesizing other boron hydrides by wet chemical metathesis reactions (e.g. in THF) with corresponding metal halogenides (usually chlorides, but also bromides are possible). This method is suitable, when no metal hydrides as a starting material exist of the wanted boron hydride.
2. AU has developed a route for producing halogen free, extremely pure boron hydrides, using a metal hydride and a $BH_3{*}S(CH_3)_2$ complex. This method relies heavily on cost of the pure hydrides and the boron containing complex.
3. At Katchem, a method based also on a metal hydride and using DMS BH_3 as boron source, was developed, which leads to high purities and reaction yields.
4. In order to achieve nanosized powder grains and/or for mixing with further compounds (e.g. MgH_2 in RHC), then the desired boron hydrides were further processed by high energy milling.

The cost analysis shows the following cost structure:

- cost of the boron source
- cost for reaction, purification and drying in wet chemical processing steps (time, machinery, man power)
- cost for mechano-chemical processing is negligible compared to materials cost.

This cost structure leads to materials cost, to a large part depending on availability of industrial size production facilities and purchased amount, and ranging from 25 €/kg ($NaBH_4$) over a few hundred Euros ($LiBH_4$) to several 10,000 Euros (e.g. $Mg(BH_4)_2$). In order to further reduce the cost for boron hydrides, it would be necessary to reduce as far as possible wet chemical processing steps and as far as possible replace them by mechano-chemical processing. Furthermore, this should be done along the whole process chain, starting from the natural boron ores (e.g. B_2O_3 or $NaBO_2$) and e.g. employing metal waste for reduction of the oxides.

4.1.3.4Work package 5: Techno-economical evaluation of a combined SOFC – solid state hydrogen storage system 70

Objectives of the work package

The major objectives of WP5 was to produce a techno - economical assessment of integrating a Solide Oxide Fuel Cell (SOFC) with a solid state H_2 storage system based on boron hydrides. The respective numerical models and the associated simulation tools are developed and tested in WP5 including a thermo-chemical model of the qualified storage material, a model for the stand-alone storage tank and a model for the integrated, thermally coupled Tank – FC system. To do so, it was necessary to make use of materials data in order to optimise the tank design under different operation modes with respect to hydrogen loading and discharge behaviour, as well as heat transfer properties and tank dimensions, according to the requirements of the FC. Based on the optimised design of the tank and the heat exchange system, an integrated SOFC – metal hydride tank system should be constructed and its performance under various conditions of operation been evaluated. Especially the behaviour of the hydrogen store under cyclic loading and unloading with hydrogen should be tested and conclusions for future improvements and practical application of such integrated systems be drawn.

Task 5.1. Combined thermo-chemical simulation of materials and tank system (HZG, AU, UNITO, NCSRD)

Hydrogen desorption from metal / complex hydrides is an endothermic process that requires significant heat fluxes (in the range of 30-80kJ/mol H_2 for common hydrogen storage materials, corresponding to 4,2 - 11,1 kWh/kg H_2) to be supplied to the metal hydride tank in order to maintain the desired desorption mass fluxes. A combined thermo-chemical simulation model of a hydrogen storage tank was developed at NCSRD. After the validation of the model, it was appropriately adjusted for simulating a tank containing the Li-RHC system, using experimental thermodynamic data and an analytic kinetic model for the composite material obtained/developed by HZG, specifically for this purpose. These data were used in the simulation of the stand-alone storage tank as well as the whole integrated SOFC – tank system developed in the project as explained below.

Task 5.2 Simulation model of integrated SOFC – hydrogen storage system (HZG, AH, NCSRD)

Using the data from Task 5.1, the development of a simulation model for the complete SOFC – hydrogen storage system was initiated by NCSRD.

The results demonstrated the relative importance of different heat transport mechanisms for various H_2 storage materials. It was also shown that radiation substantially enhances heat transfer in the tank in the case of high temperature materials, such as MgH_2, coupled with SOFC (T> 650 K), while its effect is negligible for lower temperature materials, such as LaNi5.

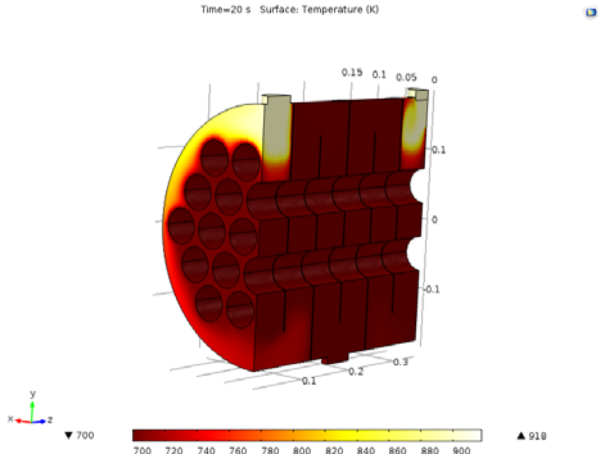


Figure 22. Temperature profiles within the helium heat exchanger designed by Helmholtz-Zetrum Geesthacht.

Building on the results of Task 5.1, NCSRD also developed a model in order to simulate and study the thermal coupling potential between SOFCs and high temperature MH alloys (including boron hydrides). Convective heating using helium as heat transfer medium between the SOFC and the MH tank was shown to be the most effective approach and as such special emphasis was placed on optimising the design of an appropriate heat exchanger system in collaboration with HZG, aiming to enhance heat transfer between the tank the fuel cell during different operational modes, including system startup, normal and shutdown operations, in order to maximize H_2 mass flux potential towards the end user.

Additionally, in a joint master thesis of HZG and Sunfire GmbH, Dresden, [18] it was shown via an ASPEN PLUS system simulation, that the optimised piping of the thermal integration scheme, shown in Figure 23, indeed leads to sufficient heat flow to the metal hydride tank for hydrogen release (Figure 24).

Task 5.2 results provided significant insight on the dynamics of the desorption process under different realistic tank/material/operating configurations, and demonstrated the relative importance of different heat transport mechanisms for various H_2 storage materials. It has been also shown that radiation substantially enhances heat transfer in the tank in the case of high temperature materials, such as boron hydrides, coupled with SOFC (T> 650 K), while its effect is negligible for lower temperature materials, such as LaNi5. It has been also possible to identify heat flux 'bottle-necks' during transient operational modes (ie. Startup), and propose optimally-designed auxiliary power sources to maintain the stability of the SOFC operation at the requested power level.

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[18] Anselm Strauch, Masterthesis, University of Duisburg-Essen, Germany, 2015

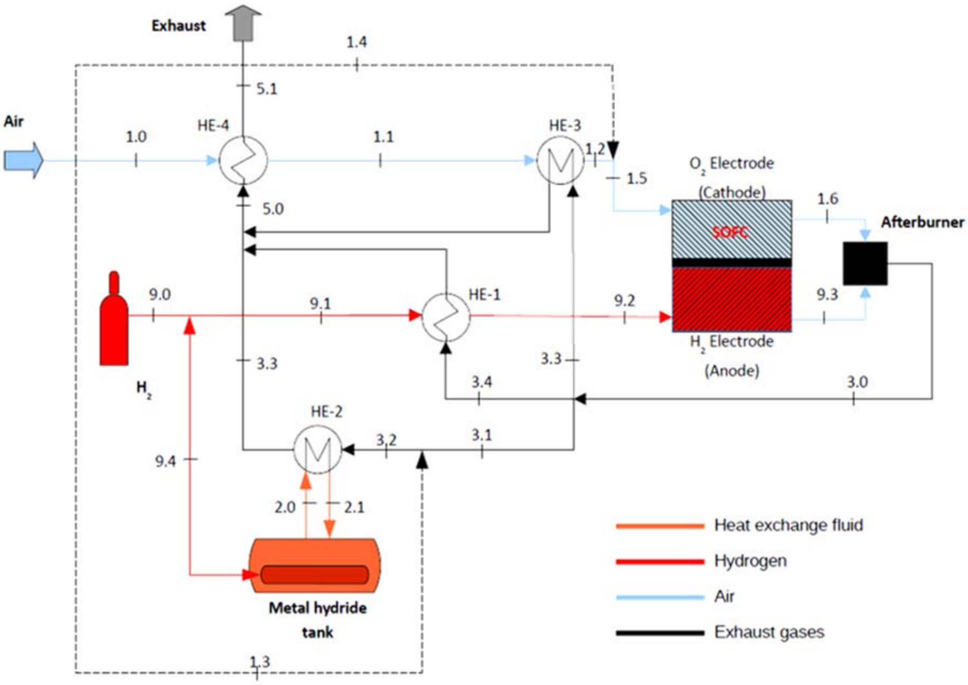

Figure 23. *SOFC – MHT integration scheme (HE: heat exchanger)*

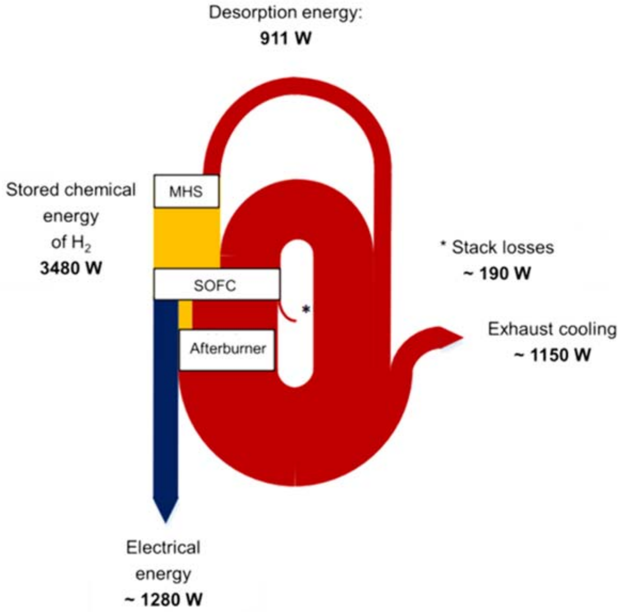

Figure 24 *Sankey diagram of the heat flows inside the integrated SOFC – metal hydride store (MHS) for the worst case scenario with* MgH_2 *(*$\Delta H \sim 75$ *kJ/(mol* H_2*), shown in Figure 23. The whole system can operated without extra electrical heating of the MHS. For the Li-RHC (*$\Delta H \sim 50$ *kJ/(mol* H_2*) instead of* MgH_2*, a smaller heat flow than 911 W, i.e. ca. 600 W, is required for hydrogen release.*
The simulation considered just the stationary case of continuous operation. Possible heat losses in the heat transfer system and of the MHS were neglected.

Task 5.3 Construction of laboratory tank and integrated system prototype, functionality tests (HZG, AH, ZOZ, NCSRD)

Based on the simulations and heat flow analysis in Task 5.2, the expected temperatures in the heat flow medium towards the metal hydride store, availability of TÜV approved heat and hydrogen resistant steels, expected loading pressure and required minimum time of hydrogen supply to the fuel cell, the following design parameters for the BOR4STORE single module tank were agreed upon in the consortium:

- max. temperature of operation (outside of steel hull) 650°C
- max. charging pressure double of that normally used (50 bar) 100 bar
- diameter of the hydrogen storage material pellets (based on analysis of their heat conductivity and necessary heat flows for hydrogen release) ca. 35 mm
- tank shall be filled in glove box under inert atmosphere ⇒
  max. length of storage tank, limited by glove box size for tank filling ca. 700 mm
- overheating of the storage material in this first prototype during welding of the storage tank for closing should be avoided. Therefore, the tank should be closed with a flange, which adds a significant amount of

weight.
In later generations of the tank, the flange shall be replaced by a 2nd welded end. But this would require developing a technique for filling the tank with the storage material before welding, and then protecting the storage material against heat, air und moisture during the welding process for closing the tank.

These boundary conditions lead to the following single module data:

- storable amount of hydrogen 50 g / 556 Nl
- amount of hydrogen storage material ca. 500 – 550 g @ 9 – 10 wt.%
- diameter of the hydrogen storage material pellets (based on internal diameter of pipe and availability of appropriate dies) 32 mm
- max. supply time for SOFC from one single module @ 15 Nl/min, i.e. max. SOFC power 37 min
- suitable alloy for storage tank tube 800 H (1.4876H)
- one end welded, one end closed by metal sealed flange
- single hydrogen inlet / outlet tube, bent to a spiral for air cooling of the released hydrogen before the flow meters (max. temperature of operation ca. 50°C)

Figure 25 BOR4STORE single module tank (ZOZ name B4S-SM). Left and write heat shieldings for hydrogen supply and take-out line (left) as well as thermocouple lines (right). Image on heat shielding box shows cooling spiral in hydrogen line and flange of proper tank module

These considerations led to a design, which in a first step was checked and approved by German TÜV Süd according to the AD2000 standard rules. In a second step, the tank then was manufactured and welded, inspected for defects, and finally underwent a pressure test with cold water at a test pressure of 325 bar, which is regarded by TÜV as being representative of 100 bar of hydrogen at 650°C tank hull temperature.

Due to the large delays in finalizing tank construction and TÜV approval, and also due to the expected high cost, it was decided by ZOZ, to supply an electrical heating for the single module tank, instead of constructing additionally a heat transfer system. The single module tank, surrounded by a heat shielding box (temperature of operation at surface of single module tank up to 650°C!) and the control unit for the electrical heating is currently (July 2016) installed at HZG premises. Additional measures for safety operation of the tank beyond the temperature of self-ignition of hydrogen (~ 550°C) and overpressurizing the tank module have to be installed in the Hydrogen Tank Test Facility at HZG, before all safety measure can be approved by the HZG safety engineers and the proper testing of the tank can start.

Task 5.4 Testing of integrated system prototype (HZG, **AH**, ZOZ, NCSRD)

Following an evaluation of the possibilities offered by the various suppliers, a 100 W_{el} (Ubocell) system produced by Almus AG was initially selected. However its preliminary assessment, also based on a thorough system analysis study using the numerical tools developed within Tasks 5.1 and 5.2, showed that it cannot support in a self-sustainable and stable mode the thermal integration with the developed hydrogen storage tank due to the small flow of the exhaust gases which were not enough for heating the MH bed at the required level to trigger hydrogen desorption.

Based on these considerations, finally a 1 kWel SOFC (Figure 26) was purchased from Sunfire GmbH as the most suitable and viable solution. It has a maximum power output of 1200 W_{DC} and can operate continuously for at least 5000 hours.

Based on cost of the single module tank and after a preliminary cost estimate, leading to cost of more than 100,000 Euro for a 1 kg hydrogen store, ZOZ took the decision not to build that tank (design draft in Figure 27), since it was beyond their planned BOR4STORE budget. Additionally, estimates for construction of a heat transfer system, based on transferring heat from the SOFC outgas via a heat exchanger and a heat exchange medium, guided towards the hydrogen store, yielded cost far beyond the foreseen budget for this 1st design and being as expensive as each, SOFC and multimodule hydrogen tank).

Figure 26. 1 kWel SOFC purchased by AH from SUNFIRE GmbH, in HZG Tank Test Facility

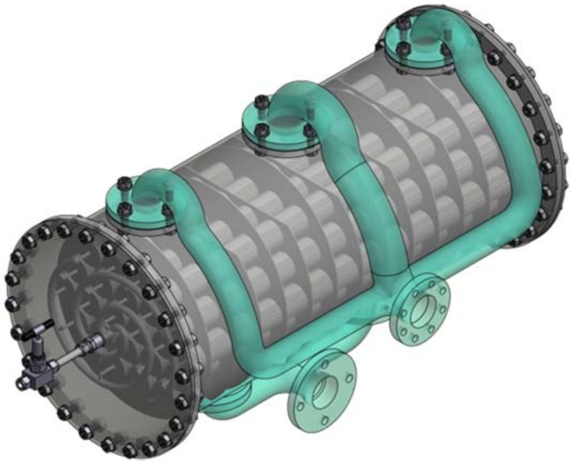

Figure 27 Multimodule tank design draft from HZG. Pressurised single tank modules (designed for 650°C and 100 bar) with welded ends. Outer hull contains heat transfer medium only and is designed for 650°C and 0.5 bar overpressure, closed by flanged ends for easy mounting of the single modules. Vertical plates guide the heat transfer medium around single tank modules.

Thus, at the end of the BOR4STORE project, it was decided by ZOZ and HZG, to build and test the single module tank, based on own resources after the end of the project. At the time of writing this report, the tank installation in the HZG Tank Test Facility is waiting for approval by the safety engineers.

Task 5.5 Techno-economical evaluation of integrated system prototype (HZG, **AH**, ZOZ, KAT, AU, UNITO, NCSRD).

(i) Design considerations

The advantage of the modular concept and tubular heat exchanger design (c.f. Figure 27) is its easy scalability and rather easy manufacturability, when compared to designs with internal heating / cooling pipes, embedded in the metal hydride, radiative heat transfer from the SOFC or heat pipes. The latter two options require special modifications of the SOFC stack itself and are expected to be difficult to be scaled up for hydrogen stores with larger sizes, whereas heat transfer from a heat exchanger in the exhaust gas system of the SOFC via a heat transfer medium in a pipe just is limited by the available heating power of the heat exchanger.

For achieving the desired storage capacity, and considering the available heat flow from the SOFC heat exchanger, simply a suitable number of single tank modules and/or longer tubes are to be united in a common shell for the heat transfer medium. Its size and thus the number of single tank tubes is limited by the available heat flow from the heat source only, neglecting heat losses to the environment by radiation or convection. Of course, these can be minimized by a proper shielding of the whole store. In order to achieve still higher storage capacity, several of these multimodule tanks have to be run in a sequence, and the heat transfer medium simply switched from one of the tanks to the next, when one multimodule tank is empty. In that way, it is in principle possible, to have tanks, which are supplying the SOFC with hydrogen, whereas others are already recharged again, thus guaranteeing a continuous supply of the SOFC.

This easy switching from supplying one tank with heat, until it is empty from hydrogen, to supplying the next, full tank with heat, is only possible with a heat transfer medium, but no other technique.

(ii) Estimates of achievable volumetric and gravimetric capacity after design optimization

As can be seen from Deliverable 5.3., the gravimetric and volumetric capacity of the single module tank (Figure 25) is far from the targets of 4 wt.% and >40 g H_2/l tank volume. This is due to several factors

1. The single module tank is the first of its kind, thus basically neither weight nor volume optimized. This remains to be done in follow-up generations of the tank.
2. The single module tank is to be operated beyond the self ignition temperature of hydrogen and surrounded by ambient air. Therefore, the prime design directive was safety against hydrogen release, meaning

a. employing high temperature and hydrogen resistant steel alloy 800H,
b. being on the safe side with the tank wall thickness,
c. using a heavy flange for safe closing of the tank under argon, thus protecting the hydrogen storage material.

Thus, this single module tank just reaches at a capacity of 50 g of hydrogen, a weight of 25.5 kg (including flange, weighing a little bit less than 20 kg), a weight of the storage material of ca. 500 g, and a volume at a length of 700 mm and 48 mm diameter (V = 1,268 l):

- gravimetric capacity 0,20 wt.% (including flange) or 0,99 wt.% (excluding flange)
- volumetric capacity 39 g H_2/l (excluding flange thickness and diameter, since that volume is not representative for the tank module, but only the tube volume)

In a weight optimized multimodule tank, a higher weight related capacity could be achieved obviously by reducing the wall thickness of the tank tubes, which currently are designed for 100 bar internal pressure at 650°C. I.e. by reducing the temperature of operation and internal pressure, significant increases of gravimetric capacity could be achieved, whereas due to the parallel tube design further increases in volumetric capacity will be rather limited. A reduction of the wall thickness from currently 7.14 mm to 3 mm would result in the following capacities:

- gravimetric capacity ca. 2,3 wt.% (weight of welded ends of outer hull neglected)
- volumetric capacity ca. 35 g H_2/l (volume of welded ends of outer hull neglected)

Since the exact design of an application scale store heavily relies on the way, how it is constructed as well as on the heat transfer system, it is impossible to calculate the exact capacity. Therefore these numbers should be taken as being indicative only. But it is clear, that it will be nearly impossible, to achieve higher densities, as the end caps of the outer hull for the heat transfer medium as well as any piping, valves etc. are still neglected in the calculation.

Cost analysis

As mentioned above, the building of the 1 kg H_2 multimodule prototype system was estimated by ZOZ with cost of more than 100,000 Euros. In series production of the single module tanks, the manufacturer offered a nearly 50% decrease of manufacturing cost per single module, and it can of course also be expected, that the prices for the special alloy 800H steel will be lower, when purchasing larger amount of the steels. But it can also be estimated, that it will be extremely difficult, if not impossible, to reach under these conditions of operation the FCH JU target cost of 500 €/kg of stored hydrogen.

Further cost decreases will only be possible by limiting the tank temperature to ca. 450°C (which is required by the Li-RHC hydrogen storage material) and the internal loading pressure to e.g. 50 bar (which would be sufficient for acceptable fast loading of the Li-RHC storage material).

But since also it is not foreseeable, if and how storage material cost can be decreased significantly below 1500 €/kg of stored hydrogen (c.f. Deliverable 4.8), it seems not to be realistic (like with all other hydrogen storage technologies– at least to our knowledge), to reach the FCH JU target cost of 500 €/kg of stored hydrogen with a boron hydride based hydrogen storage tank, operating at temperatures higher than 300°C.

Of course, the rather low loading pressure of e.g. 50 bar (compromise between acceptable fast loading and low loading pressure) gives another cost advantage in cases, where pressurizing of the hydrogen before loading is not necessary any more. This is the case e.g. when directly loading from a high pressure electrolyser.

In that case, immediately the high cost for CAPEX of the compressor (and maybe also cost for a back-up compressor, to achieve highest reliability) as well as OPEX (electricity and especially maintenance) could be saved. Purchasing cost for compressors (depending on capacity) easily reach significantly more than 50,000 Euro (example for a 50 bar, 3 kg H_2/H compressor, suitable for a 100 kW electrolyser;), which – together with its OPEX and cost for the compressed hydrogen store - has to be balanced by the extra cost for the metal hydride and the heat exchanger system, when comparing to compressed hydrogen storage.

Potential Applications of boron hydride based metal hydride tank – systems

From the remarks above it is clear, that boron hydride based metal hydride tank systems have to find a very special market niche with the following conditions:

- available heat source at a level to at minimum 450 – 500°C in order to avoid extra heating by electricity of burning hydrogen of the hydrogen storage tank and thus losing capacity;
- need for a storage capacity of > 30 g H_2/l at a charging pressure of max. 50 bar
- possibility for avoiding CAPEX and OPEX for compression for balancing cost for the store and heat exchange system.

The need for the high temperature of operation limits the field of application to those, where hydrogen is to be stored,

- for supply of SOFC's and other high temperature applications (MCFC, ICE and turbines);
- for integration with SOECs;
- especially for integration with reversible SOFC/SOEC, i.e. rSOC systems, where advantage of a) the low charging pressure and abstinence of compression, and b) the reaction heat during charging for supplying the necessary heat of evaporation to the water in steam electrolysis, could be taken.
- eventually for storage of hydrogen from solar thermal processes (heat!), but which would require extra compression.

Fields of application obviously then include net independent power supplies, “hydrogen batteries” (i.e. a hydrogen based power-to-power systems) for weekly, monthly and maybe seasonal energy storage, compact hydrogen storage for applications with limited space at rather low pressures, e.g. inside of residential and office buildings, on wind energy platforms, inside of farm buildings etc.

4.1.4 Potential impact (including the socio-economic impact and the wider societal implications of the project so far) and the main dissemination activities and exploitation of results

4.1.4.1 Potential impact and Exploitation of Results

The impact of the results, obtained in BOR4STORE, can be grouped in 3 categories:

1. Scientific Impact

BOR4STORE has created a broad experimental and theoretical data base on a wide range of boron hydride based materials, which were investigated in the project. This database (e.g. on microstructures, phase changes and reaction schemes, but also on routes for materials synthesis and processing) will be extremely useful in future projects not only on hydrogen storage, but as well as for the use of boron hydride based compounds as solid state ion conductors and eventually electrode materials.

2. Technological Impact

Though no experimental results on a hydrogen storage tank could be obtained within the time frame of the project, significant progress compared to the state of the art at the beginning of the project has been made with respect to:

- A thermo-chemical simulation model of an thermally integrated SOFC - metal hydride store has been established, allowing the computer based study of different options for heat management of the store (e.g. geometrical arrangement of the tubes inside the metal hydride tank and their intrinsic construction) and heat transfer from the heat source (e.g. radiative and convective heat transfer).
- During construction of the prototype single module tank, a large knowledge base on suitable tank geometries (related especially with heat conductivity of the storage material), usable steels, allowed for different temperatures of operation under hydrogen pressure, and the necessary steps to obtain approval of the authorities for operation as a pressurized container has been obtained.
- Deficits in the technical guidelines could be identified. E.g. there are simply no technical guidelines nor codes and standards nor safety rules on using metal hydride stores for stationary applications at temperatures higher than 100°C. ISO 16111:2008 defines only the requirements applicable to the material, design, construction, and testing of **transportable** hydrogen gas storage systems, referred to as “metal hydride assemblies” (MH assemblies) which utilize shells not exceeding 150 l internal volume and having a maximum developed pressure (MDP) not exceeding 25 MPa (250 bar).

3. Economic Impact and exploitation of results

The economic impact of the BOR4STORE project ist

All research institutes will use the knowledge acquired in BOR4STORE for future research activities, targeted at further improving the materials investigated in BOR4STORE for use in hydrogen storage, but also e.g. as solid state ion conductors for rechargeable batteries.

Katchem developed in BOR4STORE new routes for synthesis of boron hydride based compounds, widening their product portfolio to compounds like $Ca(BH_4)_2$ and $Mg(BH_4)_2$, including isotopically labelled variants.

For ZOZ, the design, construction and modification of their high energy mills with respect to processing of BOR4STORE materials brought new technological knowledge and opens up new fields of applications for their milling technology, not necessarily with hydrogen storage materials, but with all oxygen and/or moisture sensitive materials, which have to be processed under inert atmosphere completely.

AH, operating to their own selfunderstanding as a system integrator, broadened their knowledge base on possibilities of the use of metal hydride stores. But no specific impact e.g. on the portfolio of AH activities is foreseeable.

With respect to the metal hydride tank design, the economic impact is currently not foreseeable, as still significant technological hurdles have to be overcome and experimental data be obtained, before fields of application can be identified, where this hydrogen storage technology can be competitive.

Currently, the economic impact of BOR4STORE on e.g. creating new jobs at the industrial partners is not foreseeable.

4.1.4.2Main Dissemination Activities

The main dissemination activities of BOR4STORE consisted of scientific publications in high ranked journals, oral presentations and posters at conferences and workshops, as well as participation at trade fairs. They are listed in the following.

Written publications in scientific journals are listed in SESAM.

Other dissemination activities

Keynote Lectures

HZG
- Dornheim, M.; Jepsen, J.; Pistidda, C.; Karimi, F.; Gosalawit-Utke, R.; Puszkiel, J.; Lozano, G.; Bonatto Minella, C.; Boerries, S.; Bellosta von Colbe, J.; Herbst, N.; Horstmann, C.; Taube, K.; Klassen, T.: Hydrogen Storage based on Complex Hydrides and Reactive Hydride Composites: Materials and Systems. International Symposium on Metal-Hydrogen Systems, MH 2012. Kyoto (J), 21.-26.10.2012, 2012.
- Dornheim, M., 19th World Hydrogen Energy Conference 2012 – “Hydrogen Storage Materials and Systems” Symposium

ZOZ
- D. Yigit, et al., „EU-Project Bor4Store: Development of a Boron Hydride based integrated SOFC – Metal Hydride Tank System”, OZ-15 - 8th German-Japanese | 8th International Symposium on Nanostructures, March 1-3, 2015, Kusatsu/Kyoto, Japan

AU
- Torben Jensen, “New materials for hydrogen storage“, EPDIC 13 - The European Powder Diffraction Conference, Microsymposia MS05-K2, October 28-31, 2012 Grenoble, France, Invited keynote lecture.

IFE
- Bjørn C. Hauback, Stefano Deledda, Christoph Frommen, Magnus H. Sørby, “Structural studies of complex hydrides,” Hy-SEA, Brasil, 26-30 October 2014. Invited keynote lecture
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Empa
- A. Borgschulte, ”A ten years’ time travel through the research on hydrogen storage”, keynote lecture, Final meeting of the ACTS Sustainable Hydrogen, 25 -27 November 2013, De Reehorst in Ede, NL

NCSRD
- A. Ampoumogli, D. Giasafaki, Ch. Tampaxis, G. Charalambopoulou, A. Stubos, Th. Steriotis, “Hydrogen storage in solids with the use of nanoporous carbon supports and scaffolds”, Euro-Mediterranean Hydrogen Technologies Conference - EmHyTeC2014, 9-12 December 2014, Taormina, Italy.

Invited lectures

HZG
- Dornheim, M.; E-MRS 2015 Fall Meeting Symposium, Warshaw, Poland, 15-18 September 2015
- Dornheim, M.; Gordon Research Conference on Hydrogen-Metal Systems, Easton, MA, USA, 12-17 July 2015
- Pistidda, C., “Metal hydrides for H storage”, IAMNano 2015, 8-10. July 2015, Hamburg, Germany
- Dornheim, M.; International Conference on Hydrogen Storage Embrittlement and Applications, Rio de Janeiro, Brasil, 26.-30.10.2014
- Dornheim, M.; “10th International Conference on Diffusion in Solids and Liquids (DSL 2014) special session Hydrogen-Related Kinetics in Materials “, Paris, France, 23.-27. Juni 2014
- Dornheim, M.; “International Discussion on Hydrogen Energy and Applications : im Workshop “Solid hydrogen storage: links between academia and industry” , Nantes, France, 12.-14. Mai, 2014
- Dornheim, M.; “CIMTEC 2014 – 6th Forum on New Materials” in Montecatini Terme, Tuscany, Italy, June 15-20, 2014
- Dornheim, M.; Barkhordarian, G.; Jepsen, J.; Pistidda, C.; Karimi, F.; Boerries, S.; Bergemann, N.; Werner, T.; Busch, N.; Metz, O.; Horstmann, C.; Taube, K.; Bellosta von Colbe, J.; Klassen, T.; Bormann, R.: “Hydrogen Storage based on Light Weight Metal and Complex Hydrides and Reactive Hydride Composites“, 20th International Symposium on Metastable, Amorphous and Nanostructured Materials, ISMANAM 2013. Turin (I), 30.06.-05.07.2013, 2013.
- Dornheim, M.; Jepsen, J.; Pistidda, C.; Karimi, F.; Boerries, S.; Busch, N.; Metz, O.; Horstmann, C.; Taube, K.; Bellosta von Colbe, J.; Klassen, T.: “Materials and Systems for Hydrogen storage“. I²CNER Annual Symposium and the International Workshop 2013. Fukuoka (J), 28.-31.01.2013, 2013.
- M. Dornheim, J. Bellosta von Colbe,“Hydrogen Storage: Materials and Systems”, ECM 27 conference, August 7th, 2012, Bergen, Norway.
- José M. Bellosta von Colbe, G. Lozano, T. Klassen, M. Dornheim, “Material aspects in complex hydride based hydrogen storage tanks”, Expert Meeting of Task 22 of the IEA-Hydrogen Implementing Agreement, Palais Prinz Carl, Heidelberg, Germany, May 6 – 10, 2012

AU

- Torben Jensen, “Hydrogen containing solids - new perspectives“, University of Geneva, Switzerland, 2013, 24. September.
- Torben Jensen, “Gas-solid reactions and novel hydrogen storage materials investigated by in-situ SR-PXD, Structural and *in situ* materials science at beamline P02.1“, PETRA III Germany, 12-13. Sept. 2013.
- Torben Jensen, “Synthesis of new materials, structural and chemical characterization“, ‘Kickoff Meeting of Task 32 “Hydrogen-based energy storage” of the IEA-Hydrogen Implementing Agreement, Club Magic Life Candia Maris Imperial Hotel, Heraklion, Crete, Greece, 21-25 April 2013.
- Torben Jensen, “Energy storage materials – hydrogen – batteries – nanoconfinement“, Korea Institute of Science and Technology (KIST), Korea, Seoul, 28/2 2013).
- Torben Jensen, “Energi Materials Science at AU“, Korean-Danish Strategic Research Cooperation, Workshop arragnged by The Korea Research Council of Fundamental Science and Technology (KRCF) and the Danish Council for Strategic Research, Hotel President, Seoul, 26/2 2013
- Torben Jensen, “Mixed-Anion and Mixed-Cation Borohydrides“, International Symposium on Metal-Hydrogen Systems 2012 (MH2012), October 21 - 26, 2012, Kyoto TERRSA, Kyoto City, Japan.
- Torben Jensen, 2.2.5 ‘Hydrogen Storage' 2nd Joint European Summer School on Fuel Cell and Hydrogen Technology 17th – 28th September 2012 Heraklion, Crete. Invited lectures 27/10(2 hours).
- Torben Jensen, 2.2.3 ‘Application of Hydrogen' 2nd Joint European Summer School on Fuel Cell and Hydrogen Technology 17th – 28th September 2012 Heraklion, Crete..
- Torben Jensen, “New borohydrides and nanoconfinement for energy storage, Materials for Hydrogen Storage – Future Perspectives“, 14-18 June 2012 the Norwegian Coastal Express Kirkenes – Trondheim, Norway.
- Torben Jensen, “H ydrogen Storage Materials (HN2), Novel borohydrides, Nanoconfinement“, Expert Meeting of Task 22 of the IEA-Hydrogen Implementing Agreement, Palais Prinz Carl, Heidelberg, Germany, May 6 – 10, 2012
- Torben Jensen, 'New Materials for Hydrogen Storage', 13. april 2012, Distinguished iNANO lectures, iNANO, Aarhus University, Denmark

IFE

- Bjørn C. Hauback, Stefano Deledda, Christoph Frommen, Magnus H. Sørby “Structural studies of complex hydrides” 9th International Symposium on Hydrogen and Energy, Emmetten, Switzerland, 25-30 January 2015.
- Bjørn C. Hauback, “Structural studies of complex hydrides”, Hiroshima University, Japan, December 2014.
- Bjørn C. Hauback, “Structural studies of complex hydrides”, Hokkaido University, Japan, November 2014.
- B.C. Hauback, C. Frommen, M.H. Sørby, “Structural characterisation of complex hydrides”, CIMTEC, 6th Forum on New Materials, Italy, June 2014.
- B.C. Hauback, “Structural studies of complex hydrides for hydrogen storage”, Mülheim, Germany, April 2014.
- B.C. Hauback,: “Structural studies of complex hydrides for hydrogen storage”, University of Crete, Greece, November 2013.
- B.C. Hauback, “Diffraction studies of hydrogen storage materials”, Max IV Diffraction Workshop, Malmø, Sweden, September 2013.
- S. Deledda, G. Kalantzopoulos, O. Zavorotynska, M. Guzik, B.C. Hauback, “Solid-state synthesis and characterization of boron hydride-based materials for hydrogen storage“, Invited lecture at the ISMANAM-2013, July 1-5, Torino, Italy
- B.C. Hauback, “Structural studies of hydrogen storage materials”, Summit of Materials Science and Materials Science Week, MSW2012, Sendai, Japan, November 2012
- B.C. Hauback, S. Deledda, J.E. Fonneløp, C. Frommen, S, Hino, I. Llamas-Jansa, J.E. Olsen, M.H. Sørby, “Synthesis, crystal structure and properties of novel borohydrides”. International Symposium on Metal-Hydrogen Systems, Kyoto, Japan, October 2012
- B.C. Hauback, “Energy storage – hydrogen stored in solid compounds a solution?” KIFEE meeting, Trondheim, Norway, September 2012

UNITO

- M. Baricco, “Complex hydrides for energy storage and CO_2 conversion“, ISMANAM 2015, 13. – 17.7.2015, Paris, France
- M.Baricco “Hydrogen storage materials: from material science to applications” Korea-Italy Symposium Hydrogen and Fuel Cells: Current Issues and Perspectives, Seul (Kr), April 21st, 2015
- M.Baricco “Materials for Hydrogen storage” University of Sofia "St. Kl. Ohridski" May 20th, 2014
- M. Baricco “Hydrogen-based energy storage” Kickoff Meeting of Task 32 of the Hydrogen Implementation Agreement, 21-25 April 2013, Crete, Greece.
- M. Baricco “Experimental and Theoretical Studies on Hydrogen Storage Materials“ Expert Meeting of Task 22 of the IEA-Hydrogen Implementing Agreement, 6-10 May 2012, Heidelberg, Germany.

- E.Pinatel, M.Palumbo, M. Baricco "CALPHAD for Hydrogen Storage Materials", Materials for Hydrogen Storage Future Perspectives, 14-18 June 2012, Hurtigruten, Norway.
- M. Baricco, "Hydrogen Storage in Complex Hydrides", ISMANAM 2012 conference, 18-22 June 2012, Moscow, Russia.
- M.Baricco, "Metastability in Hydrogen Storage Materials", NANOMAT 2012 conference, 18 september- 2 October 2012, Sao Carlos, Brazil.
- M. Baricco, "Hydrogen Storage in Complex Hydrides", October 3rd, 2012, University of Florianopolis, Brazil.
- M.Baricco, "Metallic materials for hydrogen storage", Italian Association of Materials Science and Engineering, Lecce (Italy), September 21-24, 2014
- M.Baricco, "Fast, reliable and cost effective boron hydride based high capacity solid state hydrogen storage materials", EDEN Final Dissemination Event: "Hydrogen Storage – A key Element for Future Energy Systems", Trento, Italy, September, 25, 2015

Empa

- A. Borgschulte, Wasserstoffspeicherung - wer hat das Ei des Kolumbus, H_2BZ-Workshop "Wasserstoffspeicherung", 19 February 2013, TU Darmstadt, D

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- A. Yiotis, M. Kainourgiakis, A. Stubos, G. Charalambopoulou, "Thermal Coupling of Fuel Cell – Hydrogen Storage Systems", European Technical School on Hydrogen and Fuel Cells 2015, Heraklion, Crete, 22-26 June 2015.
- A. Yiotis, M. Kainourgiakis, Th. Steriotis, G. Charalambopoulou, A. Stubos, "Thermally coupled Hydrogen Storage - Fuel Cell Systems", European Technical School on Hydrogen and Fuel Cells 2014, 23-27 June 2014, Rethymnon-Crete, Greece.
- A. Yiotis, M. Kainourgiakis, A. Stubos, G. Charalambopoulou, "Modeling and Simulations for Integrated Hydrogen Storage - Fuel Cell Systems", European Technical School on Hydrogen and Fuel Cells 2013, Heraklion, Crete, 23-27 September 2013.
- Th. Steriotis, G. Charalambopoulou, A. Gotzias, A. Stubos, Hydrogen adsorption: a powerful tool for the surface and pore structure characterisation of nanoporous sorbents, Symposium C: Nanostructured Materials for solid state hydrogen storage, E-MRS 2013 Fall Meeting, Warsaw-Poland, 16-20 September 2013.

Oral presentations

HZG

- Taube, K., "BOR4STORE – Development of a Boron Hydride based Integrated SOFC – Hydrogen Store", ISMANAM 2015 - 22nd International Symposium on Metastable, Amorphous and Nanostructured Materials, Paris, France, July 13th - 17th, 2015
- Dornheim, M.; Jepsen, J.; Karimi, F.; Bergemann, N.; Pistidda, C.; Boerries, S.; Bellosta von Colbe, J.; Chaudhary, A.-L.; Taube, K.; Sahlmann, G.; Busch, N.; Metz, O.; Horstmann, C.; Klassen, T.: Materials and Systems for Hydrogen Storage. In: 6th Forum on New Materials: Symposium Hydrogen Production and Storage, CIMTEC 2014. Montecatini Terme (I), 15.-20.06.2014, 2014.
- J. M. Bellosta von Colbe, S. Börries, J. Jepsen, O. Metz, K. Pranzas, T. Bücherl, T. Klassen, M. Dornheim, „Investigation of hydrogen storage material's properties and behaviour towards tank design", EMRS 2013 Fall Meeting, September 19th, 2013 Warsaw, Poland
- J. M. Bellosta von Colbe, J. Jepsen, S. Börries, O. Metz, N. Busch, T. Werner, T. Bücherl, K. Pranzas, T. Klassen, M. Dornheim, "Hydrogen Storage Tanks Based on Complex Hydrides: Design, Testing and Latest Developments", EUROMAT 2013 conference, 8-13 September 2013, Sevilla, Spain.
- C. Pistidda, N. Bergemann, C. Milanese, A. Girella, S. Garroni, K. Taube, T. Klassen, M. Dornheim: Production of H_2 storage materials from waste Mg alloys, E-MRS 2013 Fall Meeting, 16.-20.09.2013.
- C. Pistidda, F. Karimi, S. Garroni, C. Milanese, L. Rude, J. Skibsted, T. R. Jensen, P. Nolis, C. Horstmann, C. Gundlach, M. D. Baró, T. Klassen, M. Dornheim: Effect of a partial replacement of CaH_2 by CaF_2 in the mixed system CaH_2 + MgB_2: Materials and Systems. International Symposium on Metal-Hydrogen Systems, MH 2012. Kyoto (J), 21.-26.10.2012.
- C. Pistidda, S. Garroni, R. Bormann, M. Dornheim, T. Klassen:"Metastability in hydrogen storage materials" ISMANAM 2013 conference, 30 June - 5 July 2013, Torino, Italy.

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- Bjarne R. S. Hansen, Claudio Pistidda, Martin Dornheim, Torben R. Jensen, "A series of *MX*B12H12-ammoniates (*MX* = Li2, Na2, Ca)", Danscatt meeting, Aarhus, Denmark, 28-29. June, 2015
- Kasper T. Møller, Bjarne R. S. Hansen, Nils Bergemann, Jose Belosta von Colbe, Martin Dornheim, Torben R. Jensen, "New Equipment for Investigation of Hydrogen Release and Uptake at high Pressure", Energy confenrence, DTU, Denmark, 14. November 2014
- Payam Javadian, Drew Sheppard, Craig Buckley, Torben R. Jensen, "Hydrogen storage properties of nanoconfined $LiBH_4$-$NaBH_4$", MH2014, Salford University, Manchester, UK

- Bjarne R. S. Hansen , Morten B. Ley, Torben R. Jensen, ”Nanoconfinement of LiBH4-KBH4 eutectic composite systems” MH2014, Salford University, Manchester, UK, 20-25. July 2014
- Bjarne R. S. Hansen, Morten B. Ley, Torben R. Jensen, ”Nanoconfinement of extremely low melting eutectic metal borohydrides: LiBH4-KBH4”, EPDIC conference, Aarhus, Denmark 16-18. June 2014
- Bjarne R. S. Hansen, Torben R. Jensen, ”Understanding Li2B12H12”, Inano meeting, Aarhus, Denmark, 16. January 2014
- Torben Jensen, “New materials for hydrogen storage“, 7th Int. Symposium Hydrogen & Energy, Seminar- und Wellnesshotel Stoos, Switzerland, January 21–25, 2013.

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- S. Deledda, Saldan, I.; Hino, S.; Humphries, T. D.; Zavorotynska, O.; Chong, M.; Jensen, C. M.; Hauback, B. C., “Structural Changes Observed during the Reversible Hydrogenation of Mg(BH4)2 with Ni-Based Additives”, 9th International Symposium on Hydrogen and Energy, Emmetten, Switzerland, 25-30 January 2015.
- O. Zavorotynska, G.Li, M.Matsuo, S. Deledda, S.Orimo, B.Hauback, “H-D exchange in $Mg(BH_4)_2$” at 9th International Symposium on Hydrogen and Energy, Emmetten, Switzerland, 25-30 January 2015.
- Bjørn C. Hauback, Stefano Deledda, Christoph Frommen, Magnus H. Sørby, Olena Zavorotynska “Metal borohydrides as hydrogen storage materials” FC EXPO 2014, FC Academic Forum, February 2014, Tokyo Japan
- Olena Zavorotynska, Christoph Frommen, Bjørn C. Hauback, M. Sørby, Stefano Deledda, “Metal Borohydrides as Hydrogen storage materials“, 3rd national meeting on inorganic and materials chemistry Hell (Norway) October 10-11, 2013.B.C. Hauback, S. Deledda, C. Frommen, M.H. Sørby, “Metal borohydrides for hydrogen storage”. KIFEE 7th International Symposium, Kyoto, Japan, March 2014.
- O. Zavorotynska, Ivan Saldan, Satoshi Hino, Terry Humphries, Stefano Deledda and Bjørn C. Hauback “Additives in magnesium borohydride: local structure and effect on reversibility” National Meeting in Inorganic and Materials Chemistry / Lillestrøm, Norway, 29-30 October 2014
- O. Zavorotynska, Ivan Saldan, Satoshi Hino, Terry Humphries, Stefano Deledda and Bjørn C. Hauback “Additives in magnesium borohydride: local structure and effect on reversibility” 14th International Symposium on the Metal-Hydrogen Systems / Manchester, UK, June 20-25 2014
- S. Deledda, G. Kalantzopoulos, O. Zavorotynska, M. Guzik, B.C. Hauback, “Solid-state synthesis and characterization of boron hydride-based materials for hydrogen storage“, Invited lecture at the ISMANAM-2013, July 1-5, Torino, Italy

UNITO

- E.R. Pinatel, E. Albanese, B. Civalleri, M. Baricco “ Thermodynamic database for borohydrides: present knowledge and future challenges ” CALPHAD XLIV, May 31st, June 5th 2015, Loano, Italy.
- E. Albanese, B. Civalleri, M. Baricco “Tuning the Stability of Ca(BH4)2 by the Inclusion of Additives: A Computational Study” MH2014, 14th International symposium on Metal-Hydrogen Systems, 20-25 July 2014 Salford, Manchester, United KingdomElisa
- J.G. Vitillo, O. Zavorynska, S. Deledda, S. Bordiga, B.C. Hauback, M. Baricco “Spectroscopic and Structural Characterization of γ-Mg(BH4)2 Thermal Decomposition: Vacuum vs. Hydrogen Atmosphere” MH2014, 14th International symposium on Metal-Hydrogen Systems, 20-25 July 2014 Salford, Manchester, United Kingdom.
- E.R. Pinatel, E. Albanese, B. Civalleri, M. Baricco “ Thermodynamics of Borohydrides-based Materials Coupling ab-initio and Calphad Methods ” MH2014, 14th International symposium on Metal-Hydrogen Systems, 20-25 July 2014 Salford, Manchester, United Kingdom
- E.R. Pinatel, E. Albanesa, B. Civalleri, M. Baricco “Thermodynaic modelling of Borohydrides for hydrogen storage” CIMTEC 2014 6th Forum on New Materials, 15-19 June 2014, Montecatini Terme, Italy.
- J. G. Vitillo, O. Zavorynska, S. Deledda, S. Bordiga, B. C. Hauback, M. Baricco, ”Spectroscopic and Structural Characterization of g-Mg(BH4)2 Thermal Decomposition: Vacuum vs. Hydrogen Atmosphere”, “14th International Symposium on Metal-Hydrogen Systems”, Salford, United Kingdom, July 20-25, 2014.
- B. Civalleri, E. Albanese, M. Corno, P.Ugliengo, M. Baricco "Ab-intio modelling of metal boron hydrides" NIS Colloquium Materials for Hydrogen Storage, February 15th, 2013, Torino, Italy.
- E. Albanese, B. Civalleri, M. Baricco ”Ab-initio modelling of metal boron hydrides as hydrogen storage materials” IX Convegno INSTM sulla Scienza e Tecnologia dei Materiali, June 30 - July 3, 2013, Bari, Italy.
- E.R. Pinatel, M. Corno, P. Ugliengo, M. Baricco “Metastability in hydrogen storage materials” ISMANAM 2013 conference, 30 June - 5 July 2013, Torino, Italy.
- B. Civalleri, E. Albanese, M. Corno, P. Ugliengo M. Baricco “Ab-initio modelling of metal boron hydrides as hydrogen storage materials “ EUROMAT 2013 conference, 8-13 September 2013, Sevilla, Spain.

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- N. Stadie, E. Callini, A. Borgschulte, A. Züttel, "Supercritical Nitrogen Processing: a Route to “Clean” Decomposition of γ-$Mg(BH_4)_2$", Empa, Dübendorf, Switzerland, 13.1.2014
- N. Stadie, A. Borgschulte, A. Züttel, "Thermodynamic Analysis of High Surface Area Materials for Energy Storage Applications", Department of Chemical Engineering, University of Bath, UK, 22.1.2014

- N. Stadie, E. Callini, R. Delmelle, A. Borgschulte, A. Züttel, "The Mystery of Diborane Evolution During the Decomposition of γ-$Mg(BH_4)_2$", 8th Hydrogen & Energy Symposium, Zhaoqing, China, 17.2.2014
- N. Stadie, "Designing Porous Materials for Clean Energy and Beyond", Laboratory of Inorganic Chemistry, ETH Zürich, Switzerland, 14.6.2014

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- A.G. Yiotis, M.E. Kainourgiakis, L. Kosmidis, G.C. Charambopoulou, A.K. Stubos, Thermal Coupling Potential of SOFCs with Metal Hydride storage tanks", Euro-Mediterranean Hydrogen Technologies Conference - EmHyTeC2014, 9-12 December 2014, Taormina, Italy.
- A. Gotzias, A. Ampoumogli, D. Giasafaki, G. Charalambopoulou, Th. Steriotis, Combining experiments and simulations for studying hydrogen sorption in nanoporous carbons, E-MRS 2015 Fall Meeting, Warsaw-Poland, 15-18 September 2015.

Posters:

HZG

- Pistidda, C., "Hydrogen storage systems from waste alloys", Gordon Research Conference on Hydrogen-Metal Systems, 7-12 July 2015, Stonehill College, Easton, MA, USA
- J. Bellosta von Colbe, G. Capurso, A. Strauch, K. Taube, O. Posdziech, T. Klassen and M. Dornheim. „Integration of a Li-RHC Tank with an SOFC: a simulation", Hydrogen-Metal Systems Gordon Conference, 12.-17.7.2015, Easton, USA.
- G. Capurso, J. Bellosta von Colbe, N. Gupta, D. Yigit, F. Pendolino, M. Melnichuk, C. Milanese, A. Girella, K. Taube, T. Klassen, M. Dornheim. "First-ever Industrial Scale Produced Boron-Based Reactive Hydride Compounds for Hydrogen Storage", Gordon Research Conference on Fundamental Aspects of Hydrogen Interaction with Materials and Novel Energy Application. Easton (MA), July 12-17 2015.
- K. Taube, J. Bellosta von Colbe, G. Capurso, J. Jepsen, C. Pistidda, A. Yiotis, M. Kainourgakis, A. Stubos, D. Yigit, H. Zoz, T. Klassen, M. Dornheim, "BOR4STORE – Development of a Boron Hydride Based Integrated SOFC – Metal Hydride Tank System", 9th Int. Symposium Hydrogen & Energy, 26.-30.1.2015, Emmetten, Switzerland
- Taube, K.; Pistidda, C.; Dornheim, M.; Mesa Velez-Bracho, V.; Escudero Avila M.T.; Lucero Martinez, C.; Palomino Marin, R.; Zoz, H.; Yigit, D.; Kriz, O.; Keder, R.; Krovacek, M.; Jensen, T.R.; Richter, B.; Javadian, P.; Deledda, S.; Hauback, B.; Zavorotynska, O.; Baricco, M.; Bordiga, S.; Civalleri, B.; Albanese, E.; Zuettel, A.; Borgschulte, A.; Stadie, N.; Charalambopoulou, G.; Stubos, A.; Steriotis, T.: "BOR4STORE: Fast, Reliable and Cost effective Boron hydride based high capacity Solid state Hydrogen Storage Materials". Gordon Research Conference on Hydrogen-Metal Systems, Hydrogen Interactions in Energy Storage. Lucca (I), 14.-19.07.2013, 2013.
- C. Pistidda, N. Bergemann, O. Metz, N. Hort, K.Taube, T. Klassen, M. Dornheim: "Production of H_2 storage materials from a waste Mg–10wt%Gd alloy". Gordon Research Conference on Hydrogen-Metal Systems, Hydrogen Interactions in Energy Storage. Lucca (I), 14.-19.07.2013, 2013.
- Taube, K.; Pistidda, C.; Dornheim, M.; Mesa Velez-Bracho, V.; Escudero Avila M.T.; Lucero Martinez, C.; Palomino Marin, R.; Zoz, H.; Ren, H.; Kriz, O.; Keder, R.; Jensen, T.R.; Deledda, S.; Hauback, B.; Baricco, M.; Bordiga, S.; Civalleri, B.; Zuettel, A.; Charalambopoulou, G.; Stubos, A.: "BOR4STORE: Fast, Reliable and Cost effective Boron hydride based high capacity Solid state Hydrogen Storage Materials".International Symposium on Metal-Hydrogen Systems, MH 2012. Kyoto (J), 21.-26.10.2012, 2012.
- J. Jepsen, J. M. Bellosta von Colbe, T. Klassen, M. Dornheim, „Scaled up $LiBH_4/MgH_2$ composite storage system as new promising hydrogen storage" (submitted and accepted), International Symposium on Metal-Hydrogen Systems, Kyoto, Japan, 2012

AH

- T. Guerrero, D. Márquez, R.Domínguez, M. T. Escudero., "Thermal integration possibilities with SOFC exhausts gases and heat transfer" European Hydrogen Energy Congress EHEC 2014, 12-14 March 2014, Seville – Spain.

KATCHEM

- R. Keder, D. Fukala, M. Krovacek, T. Jelinek, O. Kriz, B. Richter, T. R. Jensen, C. Pistidda, K. Taube, M. Dornheim, "Synthesis of $Ca(BH_4)_2$ as a potential material for hydrogen storage", EuroBoron 6, 8-13th September 2013, Radziejowice, Poland.

IFE

- O. Zavorotynska, M.N. Guzik **,** J. G. Vitillo **,** I. Saldan **,** S. Deledda **,** B.C. Hauback **"**Decomposition of Magnesium Borohydride with Cobalt Additives: An in-situ Synchrotron X-ray Study Combined with Raman Spectroscopy" SYKNØYT Users meeting, 19-20 January 2015, Stavanger, Norway
- B.C. Hauback, S. Deledda, C. Frommen, M. Sørby, O. Zavorotynska «Solid State Hydrogen Storage Materials: Metal Borohydrides», FC EXPO Academic Forum, February 2014, Tokyo Japan

- Olena Zavorotynska, Stefano Deledda, Bjørn C. Hauback, “Magnesium borohydride as hydrogen storage material“, Third Annual Niels Bohr International Academy Workshop on ESS Science: Crossing space and time domains with SAS and QENS, Copenhagen (Denmark) June 24-28, 2013
- Olena Zavorotynska, Satoshi Hino, Ivan Saldan, Terry Humphries, Stefano Deledda, Bjørn C. Hauback, “Effect of additives on hydrogen sorption in $Mg(BH_4)_2$“, Gordon Research Conference on Metal-Hydrogen Systems, Barga (Italy) July 14-18, 2013
- Olena Zavorotynska, Stefano Deledda, Bjørn C. Hauback, “Characterization of lightweight metal borohydrides with vibrational spectroscopy“, Gordon Research Seminar on Metal-Hydrogen Systems, Barga (Italy) July 13-14, 2013
- Olena Zavorotynska, Stefano Deledda, Bjørn C. Hauback, “Effect of additives on hydrogen sorption in $Mg(BH_4)_2$“, Joint EDEN-HYPER-SSH2S-BOR4STORE Workshop on hydrogen storage, Santa Cruz, Tenerife (Spain), October 2, 2013

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- Bjarne R. S. Hansen, Anna-Lisa Chaudhary, Claudio Pistidda, Martin Dornheim, Torben R. Jensen, ”Ammoniation of MxB12H12 (Mx = Li2, Na2, Ca)”, Gordon Research Conference “Hydrogen Metal Systems”, Stonehill College, Easton, MA, USA, 12-17. July 2015
- Bo Richter, Morten B. Ley, Torben R. Jensen, “Metal borohydrides; new methods and materials“,Joint EDEN-HYPER-SSH2S-BOR4STORE Workshop on hydrogen storage, Santa Cruz, Tenerife (Spain), October 2, 2013
- Payam Javadian, Torben R. Jensen, “Kinetic properties of melt infiltrated eutectic borohydride composites into high surface area scaffolds“, Joint EDEN-HYPER-SSH2S-BOR4STORE Workshop on hydrogen storage, Santa Cruz, Tenerife (Spain), October 2, 2013
- Bo Richter, Elsa Roedern, Dorthe B. Ravnsbæk, b, Yaroslav Filinchuk, Torben R. Jensen, “$Mn(BH_4)_2$: Synthesis, Polymorphism and Thermal Decomposition Pathways“, iNano Meeting, Aarhus, DK jan. 16, 2013.
- Elsa Roedern, Torben R. Jensen, “Manganese borohydride composite systems“, GRC conference, Italy, 14-19 July 2013
- Elsa Roedern, Bo Richter, Torben R. Jensen, “Hydrogen storage in metal borohydride composite systems“, BASF summer school, feb. 8 2013
- Bjarne R. S. Hansen, Dorthe B. Ravnsbæk, Carsten Gundlach, Jørgen Skibsted, Torben R. Jensen, “Reversibility in $LiBH_4$-MgH_2-Al“, GRC conference, Italy, 14-19 July 2013 and Joint EDEN-HYPER-SSH2S-BOR4STORE Workshop on hydrogen storage, Santa Cruz, Tenerife (Spain), October 2, 2013
- Bjarne R. S. Hansen, Dorthe B. Ravnsbæk and Torben R. Jensen, “Decomposition Reactions in the LiBH4-MgH2-Al composite system“,MH 2012 conference, Japan

UNITO

- Roberto Gobetto, Marcello Baricco, Michele R. Chierotti, Federico Franco, Carlo Nervi, Federico M. Paruzzo, Anna R. Wolczyk, “Synthesis and characterization of novel hydrogen storage materials”, XLIII° Congresso Nazionale della Divisione di Chimica Inorganica, Camerino (Italy), 9-12 September 2015.
- Roberto Gobetto, Federico Franco, Michele Chierotti, Carlo Nervi, Marcello Baricco, “Solid State NMR Spectra and GIPAW Plane-Wave Investigations of Hydrogen Storage Materials”, XXV° Congresso della Società Chimica Italiana, Arcavacata di Rende (CS, Italy), 7-12 September 2014.
- F. Franco, M. Baricco, M. Chierotti, R. Gobetto, C. Nervi, “From pseudopotentials to SSNMR parameters: an integrated computational and experimental study of materials for hydrogen storage“, Conference of the German, Italian and Slovenian Magnetic Resonance Societies, 9-12 September 2013, Frauenchiemsee, Germany.
- E.Albanese, B. Civalleri, M. Baricco, “Ab-initio modeling of metal borohydrides as hydrogen storage materials”, Gordon conference on Hydrogen-Metal Systems, 14-19 July 2013, Lucca, Italy.
- E.Albanese, B. Civalleri, M. Baricco, ”Ab-initio modelling of metal borohydrides as hydrogen storage materials”, IX Convegno INSTM sulla Scienza e Tecnologia dei Materiali, June 30 - July 3, 2013, Bari, Italy.
- B. Civalleri, E. Albanese, M. Corno, P. Ugliengo, M. Baricco, “Ab initio modelling of metal borohydrides as hydrogen storage materials“, XLI Congresso Nazionale di Chimica Fisica, 23-27 June 2013, Alessandria, Italy.

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- Nicholas Stadie, Andreas Borgschulte, Andreas Züttel, "The enthalpy of dehydrogenation with a focus on $Ca(BH_4)_2$: principles and techniques"“, Gordon Research Conference on Metal-Hydrogen Systems, Barga (Italy) July 14-18, 2013
- Nicholas Stadie, Andreas Borgschulte, Andreas Züttel, Olena Zavorotynska, Stefano Deledda, Bjørn Hauback, Bo Richter, and Torben Jensen, “"In-situ impurity gas analysis of (α-, β-, and γ-) Mg(BH4)2 during dehydrogenation", Joint EDEN-HYPER-SSH2S-BOR4STORE Workshop on hydrogen storage, Santa Cruz, Tenerife (Spain), October 2, 2013

NCSRD

- A. Ampoumogli, G. Charalambopoulou, Th. Steriotis, P. Javadian, B. Richter, T.R. Jensen, “Hydrogen Desorption and Cycling Properties of Eutectic Borohydrides - Mesoporous Carbons Composites”, 14th E. International Symposium on Metal-Hydrogen Systems (MH 2014), Salford, Manchester - UK, 20 - 25 July 2014.
- A. Yiotis, M.E. Kainourgiakis, G.Ch. Charalambopoulou, A.K. Stubos "Thermal coupling of high temperature metal hydride tanks with Solid Oxide Fuel Cells", International Congress on Materials and Renewable Energy (MRE 2013), 1-3 July 2013, Athens, Greece.
- D. Giasafaki, Ch. Tampaxis, A. Ampoumogli, G. Charalambopoulou, A. Bourlinos, A. Stubos, Th. Steriotis, Studying the effect of surface chemistry and metal-doping on the hydrogen storage capacity of carbon nanostructures, Symposium C: Nanostructured Materials for solid state hydrogen storage, E-MRS 2013 Fall Meeting, Warsaw-Poland, 16-20 September 2013.
- A. Yiotis, M.E. Kainourgiakis, G.Ch. Charalambopoulou, A.K. Stubos "Thermal coupling of high temperature metal hydride tanks with Solid Oxide Fuel Cells",, Joint EDEN-HYPER-SSH2S-BOR4STORE Workshop on hydrogen storage, 2 October 2013, Tenerife - Spain.

Participations at fairs

- H2Expo, Hamburg, September 2014 (HZG)

4.1.5 Address of the project public website, as well as relevant contact details.

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