

# PROJECT FINAL REPORT

**Grant Agreement number:** 226943

**Project acronym:** FLYHY

**Project title:** Fluorine Substituted High Capacity Hydrides for Hydrogen Storage at Low Working Temperatures

**Funding Scheme:** Collaborative Project

**Period covered:** from January, 1<sup>st</sup>, 2009 to December, 31<sup>st</sup>, 2011

**Name, title and organisation of the scientific representative of the project's coordinator:**

Dr. Klaus Taube  
Helmholtz-Zentrum Geesthacht GmbH

**Tel:** +49 (4152) 87 25 41

**Fax:** +49 (4152) 87 26 36

**E-mail:** klaus.taube@hzg.de

**Project website address:** [www.flyhy.eu](http://www.flyhy.eu)

## Contents:

4.1	Final publishable summary report.....	- 1 -
4.1.1	Executive summary.....	- 1 -
4.1.2	Summary description of project context and objectives. ....	- 2 -
4.1.3	Main S&T results/foregrounds .....	- 3 -
4.1.4	Work packages 1 and 2 : Materials Preparation and Characterisation .....	- 3 -
	Objectives of the planned investigations of the work packages .....	- 3 -
	Halogen substituted hydrides based on different modifications of alane .....	- 3 -
	Halogen substituted hydrides based on stable borohydrides .....	- 4 -
	Halogen substituted hydrides based on unstable borohydrides .....	- 10 -
	Halogen substituted hydrides based on Reactive Hydride Composites (RHC) .....	- 11 -
	Main scientific results .....	- 15 -
4.1.5	Work package 3: Theory and Modelling .....	- 17 -
	Objectives of the planned investigations of the work package.....	- 17 -
	Task 3.2.: Assessment of binary systems.....	- 18 -
	Task 3.3.: Assessment of multicomponent systems.....	- 19 -
	Task 3.4.: Kinetic modelling.....	- 21 -
	Main scientific results .....	- 21 -
4.1.6	Work package 4: Techno-Economical Evaluation.....	- 22 -
	Objectives of the planned investigations of the work package.....	- 22 -
	Task 4.1: Cost, benchmarking of materials.....	- 23 -
	Task 4.2: Determination of tank relevant properties.....	- 25 -
	Task 4.3. Safety.....	- 26 -
	Task 4.4. Tests in laboratory prototype tank.....	- 27 -
4.1.7	Main scientific results .....	- 28 -
4.1.8	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	- 29 -
4.1.8.1	Potential impact and exploitation of results.....	- 29 -
4.1.8.2	Main Dissemination Activities.....	- 29 -
	Publications.....	- 30 -
	Talks:.....	- 31 -
	Posters: .....	- 34 -
	Participations at fairs.....	- 35 -
4.1.9	Address of the project public website, if applicable as well as relevant contact details.	- 36 -

## 4.1 Final publishable summary report

### 4.1.1 Executive summary

FLYHY focused on tailoring of materials thermodynamics and kinetics by anion substitution in high capacity hydrogen storage materials (alane, borohydrides and Reactive Hydride Composites RHC), on employing novel paths of materials synthesis, on obtaining in depth scientific understanding by extended structural and thermodynamic characterisation and modelling, on determining tank relevant materials properties like compaction behaviour and thermal conductivity, on scaling-up materials synthesis and testing a prototype solid state hydrogen storage tank.

H substitution by more electronegative halogens F, Cl, Br, and I in a functional group or a complex changes the bond strength of the remaining elements and thereby may facilitate release and uptake of hydrogen. FLYHY investigated, whether too stable or too unstable materials could be modified such, that their stability reached the desired state (reaction enthalpy -30 to -40 kJ/(mol H<sub>2</sub>)), while retaining high storage capacity. Modified alane and RHCs were synthesised by high energy ball milling routes. For pure and modified stable and unstable borohydrides novel wet chemical routes for synthesis and combinations with ball milling were developed.

For alane, a wide range of compositions and milling parameters were studied, but no indications of fluorine substitution were observed, agreeing with our theoretical calculations. Due to a positive mixing enthalpy of AlH<sub>3</sub> and AlF<sub>3</sub>, fluorine substitution is rather unlikely. Work on alane was terminated after the first year of the project.

For pure, stable borohydrides like LiBH<sub>4</sub>, Mg(BH<sub>4</sub>)<sub>2</sub> and Ca(BH<sub>4</sub>)<sub>2</sub> new routes of wet chemical synthesis with high yield were developed. They show a high cost advantage compared to the same, commercially available materials.

In pure LiBH<sub>4</sub>, Cl, Br, and I substitution for BH<sub>4</sub><sup>-</sup> groups was found, in Ca(BH<sub>4</sub>)<sub>2</sub> only substitution by Cl and I. Substitution with the heavier halogens leads to the stabilisation of the hexagonal high temperature LiBH<sub>4</sub> polymorph down to room temperature. Substitution was observed as a solid solution with the compound containing the larger anion as the host-structure. By addition of fluorine the stability of borohydrides could be lowered significantly and hydrogen, but in some cases also other compounds like boranes, were released already below 150°. Indications of fluorine substituting for hydrogen in BH<sub>4</sub><sup>-</sup> groups were observed, e.g. in *in situ* PXD and NEXAFS data. The hydrogenation was not completely reversible, but significantly enhanced compared to the pure compounds.

For Ca, Li and Na based RHCs, effects of fluorine addition were found in all 3 systems, as a lowered dehydrogenation temperature and significantly increased reaction rates in the Ca based RHC. Double peaks in DSC and NEXAFS hint on structural changes due to fluorine, especially significant in the Ca-based RHC. Cycling of that compound lowered the onset of hydrogen desorption from ca. 300°C down to less than 250°C, but also the storage capacity of ca. 7 wt% decreased to ca. 4wt.% in the first cycle, remaining constant in the following cycles. Modelling of reaction kinetics gave a reduction of the activation energy from 160 to 115 kJ/(mol H<sub>2</sub>) upon cycling. Increasing F content in this RHC seems to lead to lower reaction enthalpy and activation energy. A value of 49 kJ/(mol H<sub>2</sub>) was estimated from DSC measurements. This behaviour could be completely explained by the reaction pathway leading to unwanted side and endproducts. Optimisation of reaction temperatures and pressures and proper additives are expected to lead to reaction pathways, which maintain the high storage capacity.

Comparison of life cycle and fuelling cost of present hydrogen storage methods showed that solid state hydrogen storage already today is competitive with compressed and liquid storage, provided that raw materials are purchased from large scale industrial suppliers in tonnage quantity and not from fine chemical suppliers in gram amounts. Effects of less purity of raw materials have to be studied in future projects. The developed materials synthesis routes and employed storage tank technology are especially suitable for manufacturing by SME's.

#### 4.1.2 Summary description of project context and objectives.

The world's primary energy needs are expected to grow by 55% from 2005 to 2030. The present energy supply is based on the limited resource fossil fuels, the use of which is causing the CO<sub>2</sub> content of the atmosphere to increase and possibly also the global mean temperature. Renewable energy sources like sun, wind or biomass are obvious alternatives to the present use of fossil fuels, but suffering from one major problem: They are unevenly distributed both geographically and over time. Most countries need to integrate several contributions of renewable energies. Therefore, a safe, cheap and efficient energy carrier is required, which can be converted e.g. to electrical energy or heat without harm for the environment. Hydrogen would be the ideal choice, but it suffers from one fundamental drawback – as hydrogen is a light gas at ambient conditions, it is very difficult to store in the density and compactness required for industrial and consumer applications.

Novel materials form the backbone of any emerging energy technology such as the hydrogen based future economy. The scientific core of FLYHY was to carry out international cutting-edge design, preparation, characterisation and application of novel materials for hydrogen storage in the solid state.

At present there is still **no hydrogen storage system available fulfilling all requirements for use especially in mobile applications simultaneously**: 1. high storage density, 2. temperatures and heats of operation compatible with PEM fuel cells, 3. high hydrogen loading and unloading rates in the range of a few minutes and 4. low system costs. FLYHY focused especially on the first three points by

- (i) exploiting findings on tailoring of materials thermodynamics by anion substitution in alane, borohydrides and Reactive Hydride Composites, in order **to achieve a breakthrough in the thermodynamic hydrogen sorption properties of these materials exhibiting the highest hydrogen capacities known at present**,
- (ii) obtaining an **in depth scientific understanding of the sorption properties** of the substituted compounds by extended structural and thermodynamical characterisation and modelling, to optimise the investigated materials,
- (iii) determining **tank relevant materials properties** like e.g. compaction and cycling behaviour,
- (iv) **scaling-up materials production** and doing first tests in a **prototype tank**.

**Tailoring of physical properties** such as thermodynamics, i.e. working temperatures, and reaction kinetics, was achieved **by adding halogens to the storage materials** and employing **novel paths of materials synthesis**.

Substitution of an element, i.e. hydrogen, with a more electronegative element in a functional group or a complex, changes the bond strength of the remaining elements and thereby may facilitate release and possibly uptake of hydrogen. FLYHY chose the most electronegative element, fluorine, as the focus of its research and also its group members in the periodic table, chlorine, bromine and iodine. By partially substituting halogens for hydrogen or functional groups like (BH<sub>4</sub>)<sup>-</sup>, the enthalpy of reaction of too stable and too unstable high capacity hydrogen storage materials should be changed to the desired range of -30 to -40 kJ/(mol H<sub>2</sub>), while retaining as much hydrogen storage capacity as possible.

For achieving the targets of FLYHY, three material systems had been selected:

- **Alane** (AlH<sub>3</sub>, theoretical storage capacity 10.1 wt%), which up to now cannot be rehydrogenated at conditions suitable for onboard loading. Unmodified alane is also thermodynamically much too unstable for practical use.
- **Borohydrides** show some of the highest theoretical gravimetric hydrogen contents (e.g. LiBH<sub>4</sub> 18.5 wt%), but for practical use are much too stable or too unstable, respectively.
- **Reactive Hydride Composites** (RHC) (reversible capacity up to 11 wt% (LiBH<sub>4</sub>+MgH<sub>2</sub>)) have the unique advantage - compared to all other methods for modifying hydrogen storage materials - that

upon reaction of two or several hydrides in the composite, an average hydrogen storage capacity together with a substantially reduced reaction enthalpy is achieved.

The objectives of the FLYHY project were to obtain also fundamental knowledge on (i) **novel routes for reproducible and safe materials synthesis**, (ii) the **influence of the modified materials structures on hydrogen sorption properties**, (iii) **assessment of the different storage materials** with regard to raw materials and production cost and necessary expense for storage tank construction with regard to tank capacity, heat management and tank safety, (iv) **storage tank relevant materials parameters** like practical storage densities and thermal conductivities of the materials, hydrogen sorption properties in larger amounts of powders, sensitivity to hydrogen purity and long term stability, (v) (if promising materials are available at milestone in month 30) **upscaled production processes as well as materials behaviour in a laboratory prototype test tank**, giving input for future improvements in the time following this project.

### 4.1.3 Main S&T results/foregrounds

#### 4.1.4 Work packages 1 and 2 : Materials Preparation and Characterisation

##### Objectives of the planned investigations of the work packages

All known high-capacity hydrogen storage materials are hampered by too high or too low thermal stability. The efforts under WP1 and WP2 aimed to substitute halides into such materials (WP1) and investigate the effects on structure and properties with emphasis on hydrogen storage performance (WP2). Four classes of materials were chosen for investigations:

- Alane,  $\text{AlH}_3$ , which is too unstable for reversible hydrogen storage.
- Stable borohydrides, especially  $\text{LiBH}_4$ ,  $\text{NaBH}_4$ ,  $\text{Mg}(\text{BH}_4)_2$  and  $\text{Ca}(\text{BH}_4)_2$ , which desorb large amount of hydrogen but at impractically high temperatures.
- Unstable borohydrides, especially  $\text{Al}(\text{BH}_4)_3$  and  $\text{Zr}(\text{BH}_4)_n$ , which are unstable at ambient conditions.
- Reactive Hydride Composites (RHCs), based on M-B-H-F systems where M = Li, Na, Mg and Ca.

Syntheses were performed in the solid state with ball milling techniques under various temperature and pressure conditions, as well as wet chemistry techniques. The materials were characterized with techniques such as in-situ and ex-situ powder X-ray/synchrotron diffraction, neutron diffraction, Differential Scanning Calorimetry, Temperature Programmed Desorption, Mass Spectroscopy, IR and Raman Spectroscopy, and manometric gas sorption measurements.

##### Halogen substituted hydrides based on different modifications of alane

Alane,  $\text{AlH}_3$ , has high hydrogen capacity (10.1 wt%, 148 g( $\text{H}_2$ )/L) and fast hydrogen release at moderate temperature, but is far too unstable for rehydrogenation from the gas phase. Stabilisation by fluorine substitution would therefore be of great practical interest.

Alane can be produced in a solid-state reaction between lithium or sodium alanate and aluminium chloride by mechanical milling at cryogenic temperature:



Substitution of hydrogen by fluoride was attempted by two different approaches. Firstly, fluorides ( $\text{NaF}$ ,  $\text{AlF}_3$  and  $\text{TiF}_3$ ) were added to the reaction mixtures above before cryomilling. This mostly led to

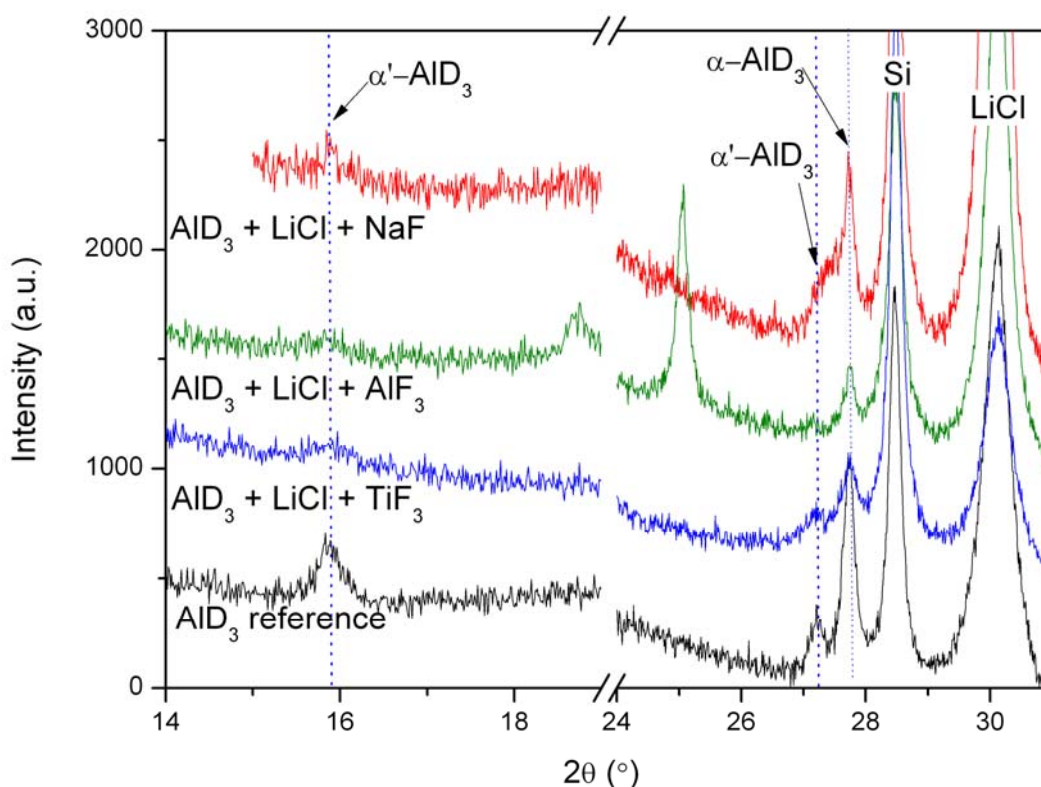


Fig. 2: PXD patterns of as-synthesised with alane and alane milled with various fluorides. The constant peak positions from alane indicate that no fluorine substitution has taken place. Si is present as an internal standard in the measurements.

unwanted side-reactions which inhibited alane formation (pure or substitute). Secondly, alane was first synthesised by cryomilling, then mixed with fluorides and cryomilled further. PXD-patterns showed no shift in the peak positions after milling (Fig. 2). This indicates that no F is substituted into the alane phases. The immiscibility of fluorine in alane is supported by theoretical calculations in WP3.

#### Halogen substituted hydrides based on stable borohydrides

##### New route for synthesis of halogen free $\alpha$ - $\text{Ca}(\text{BH}_4)_2$

A new method for synthesis of  $\text{Ca}(\text{BH}_4)_2$  with very high elemental- and phase purity was developed by Aarhus University, and is currently being patented. Powder X-ray diffractograms of the synthesis products (Fig 1.) demonstrate the viability of the method. Besides the advantage of synthesis of very pure material (e.g. for fundamental scientific investigations) the method offers a significant cost advantage compared to commercially available borohydrides.

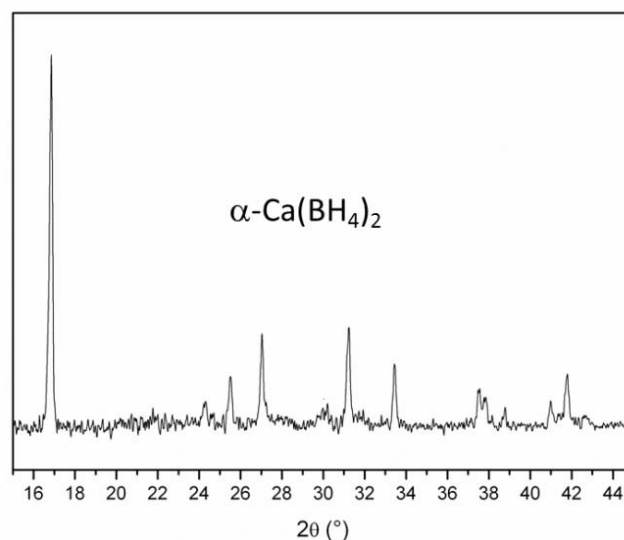


Fig. 1: Powder X-ray diffraction for as-synthesized  $\text{Ca}(\text{BH}_4)_2$ , using a novel synthesis route. Only Bragg peaks from the  $\alpha$ -polymorph are observed, i.e. this method is effective for synthesis of phase-pure materials, thus allowing for more accurate analysis of purity and thus provides better basis for e.g. determination of enthalpies of decomposition. Purity of hydrogen storage materials and consequences hereof has been a topic of wide discussion, therefore this method was developed.



### Determination of enthalpy and entropy for pure $\text{Ca}(\text{BH}_4)_2$ synthesized at University of Aarhus

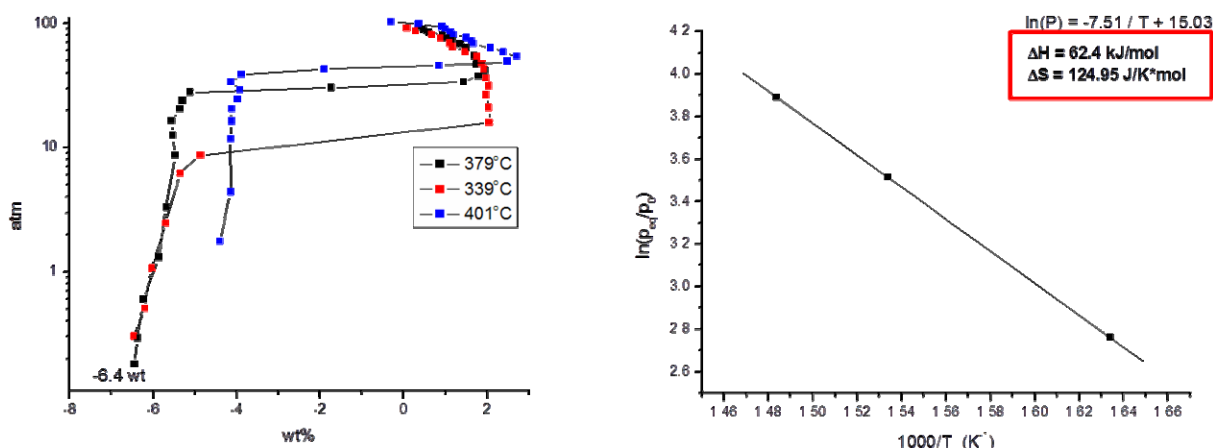


Fig. 3: PCI's of  $\alpha\text{-Ca}(\text{BH}_4)_2$  dehydrogenation and van't Hoff plot determining enthalpy and entropy of dehydrogenation.

Single phase  $\alpha\text{-Ca}(\text{BH}_4)_2$  was produced to more precisely determine the enthalpy and entropy of dehydrogenation of  $\text{Ca}(\text{BH}_4)_2$ . The material was produced so as to yield the purest possible material; a new synthesis method was developed which facilitates *i*) the production of elementally pure borohydrides and *ii*) phase-pure borohydrides. The process is transferrable to other metal borohydrides and is currently being patented by Aarhus University. Three PCI curves of  $\text{Ca}(\text{BH}_4)_2$  were obtained, at 339, 379 and 401 °C. From the PXD patterns after dehydrogenation  $\text{CaH}_2$  and  $\text{CaB}_6$  was revealed as main decomposition products (plus other phases to be identified). Thermodynamic data were extracted from a van't Hoff plot of the dehydrogenation of  $\text{Ca}(\text{BH}_4)_2$ , allowing us to determine the enthalpy ( $\Delta H = 62 \text{ kJ/mol}$ ) and entropy ( $\Delta S = 125 \text{ J/K}^\circ\text{mol}$ ) of dehydrogenation. (Fig. 3).

### Significant destabilization of metal borohydrides by addition of metal tetrafluoroborates (Li, Na, Ca)

Mixing metal borohydrides with the corresponding metal tetrafluoroborates in various relative ratios has been shown to destabilize the metal borohydride part to a significant extent. TPD-MS data (Fig. 4) measured at IFE for  $\text{LiBH}_4\text{-LiBF}_4$  mixtures (hand ground) clearly illustrate the destabilization as detection of  $\text{H}_2$ ,  $\text{B}_2\text{H}_6$  or  $\text{BF}_3$  at temperatures corresponding to the temperatures of weight losses (TGA/DTA). The new decomposition temperatures are dependent on the specific quantities of added tetrafluoroborate material. The decomposition products include crystalline  $\text{LiF}$  and amorphous  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  as observed by *in situ* synchrotron radiation powder X-ray diffraction and  $^{11}\text{B}$  MAS NMR, respectively.

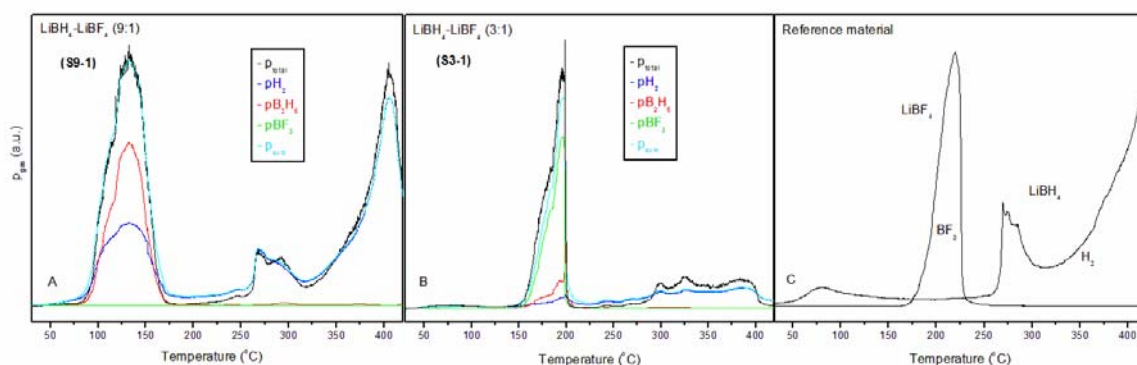


Fig. 4: TPD-MS (Temperature Programmed Desorption - Mass Spectroscopy) for  $\text{LiBH}_4\text{-LiBF}_4$  (9:1) (A) and  $\text{LiBH}_4\text{-LiBF}_4$  (3:1) (B). Reference materials are shown in (C).

The same general trend is observed for  $\text{Ca}(\text{BH}_4)_2$  -  $\text{Ca}(\text{BF}_4)_2$  mixtures (not shown); the mixtures desorb a mixture of gases at significantly lowered temperatures.  $\text{LiBH}_4$ - $\text{LiBF}_4$  mixtures are investigated in more detail (see below). For these mixtures, the effect of destabilization is significant, however, for Li and Ca the formation of other gases than  $\text{H}_2$  is detrimental for their use in hydrogen storage since cycling is rendered impossible. The effect is in good accordance with the theoretically predicted behaviour, since we would expect a strong destabilizing effect specifically from the incorporation of fluorine.

#### Fluorine substitution observed/indicated using *in situ*-SR-PXD and Rietveld refinement methods.

The  $\text{LiBH}_4$ - $\text{LiBF}_4$  mixtures were examined using *in situ*-SR-PXD techniques, thus allowing for analysing the data using Rietveld refinement. The first scans of the *h*- $\text{LiBH}_4$  polymorph were refined due to clear changes in relative intensities of the Bragg peaks, which is what we would expect to see, in order to detect fluorine substituting for hydrogen. Refinements indicate that F substitutes directly for H in the  $\text{BH}_4^-$  unit, however, this effect is observed only for the hexagonal  $\text{LiBH}_4$  polymorph, thus suggesting that substitution occurs gradually as heating and decomposition progresses (Fig. 5). Decomposition of the substituted material appears immediately as it forms. More detailed investigations are underway in order to firmly establish the occurrence of fluorine substitution.

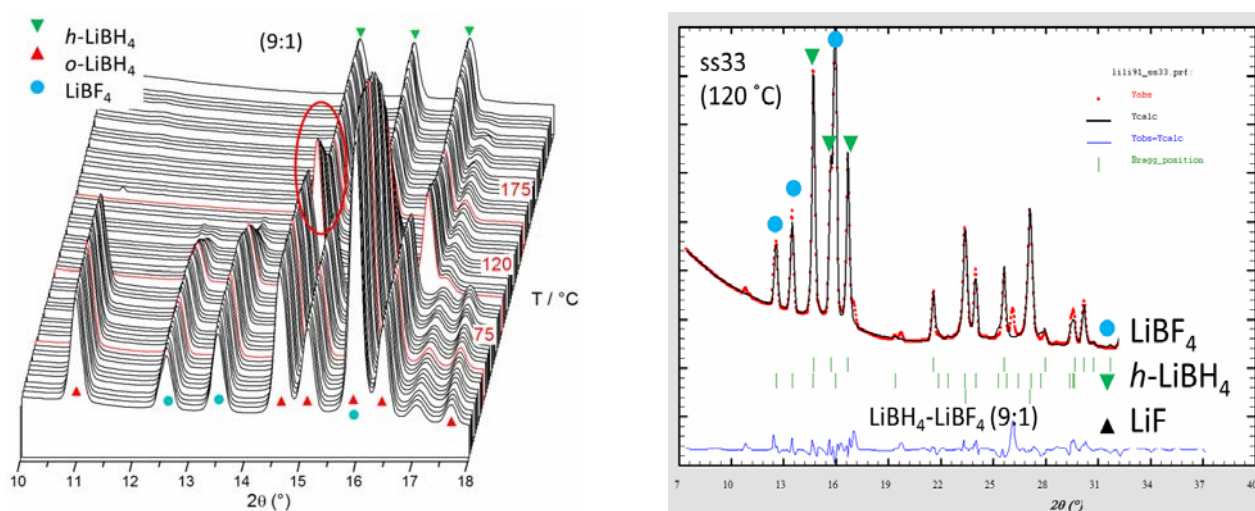


Fig. 5: *In situ*-SR-PXD data for  $\text{LiBH}_4$ - $\text{LiBF}_4$  (9:1) (left) and Rietveld refinement profile for the first scan of *h*- $\text{LiBH}_4$  in the sample (right). The red circle indicates the most clear intensity anomaly (left).

The  $\text{LiBH}_4$ - $\text{LiBF}_4$  (9:1) sample desorbs a mixture of  $\text{H}_2$  and  $\text{B}_2\text{H}_6$ , i.e. no traces of  $\text{BF}_3$  are observed in the TPD-MS. The gas release occurs approximately simultaneously with the phase transition from *o*- $\text{LiBH}_4$  to *h*- $\text{LiBH}_4$ , i.e. at  $\approx 100$  °C. For  $\text{LiBH}_4$ - $\text{LiBF}_4$  (3:1) the situation is slightly different; decomposition occurs at higher temperatures and the released gaseous species are mainly  $\text{BF}_3$  (Fig. 4, B above). This indicates two different reaction pathways depending on the added amounts of  $\text{LiBF}_4$ .

#### Improved hydrogen cyclability for $\text{NaBH}_4$ - $\text{NaBF}_4$ mixtures

Mass spectroscopy measured while decomposing  $\text{NaBH}_4$ - $\text{NaBF}_4$  (2:1) in a temperature range from *RT* to 600 °C shows a large  $\text{H}_2$ -signal and minor fractions of  $\text{B}_2\text{H}_6$  and  $\text{BF}_3$  at 300 °C (Fig. 6, A). The rehydrogenation properties of the  $\text{NaBH}_4$ - $\text{NaBF}_4$  (2:1) system were investigated using the Sieverts method (Fig. 6, B). In the 1<sup>st</sup> desorption  $\text{NaBH}_4$  (without  $\text{NaBF}_4$ ) releases 6.0 wt% in 105 hours (only the first 12 h are shown in the Figure) corresponding to 75 % of the total capacity. Rehydrogenation was performed at 450 °C and  $p(\text{H}_2) \sim 130$  bar for 24 hours. During the 2<sup>nd</sup> and 3<sup>rd</sup> dehydrogenation 0.69 wt% and 0.65 wt%  $\text{H}_2$  is released respectively (8% and 9% of the capacity). In the 1<sup>st</sup> desorption of  $\text{NaBH}_4$ - $\text{NaBF}_4$  (2:1) a release of 9.1 wt% corresponding to 86 % of the total capacity (assuming all is  $\text{H}_2$ ), is observed. During 2<sup>nd</sup> and 3<sup>rd</sup> desorption the sample releases 3.6 wt% and 3.2 wt% respectively



(i.e. 34% and 30% of the capacity, again assuming all is  $H_2$ ). Thus, the reversible capacity of the system  $NaBH_4$ - $NaBF_4$  is significantly improved compared to pure  $NaBH_4$  [1].

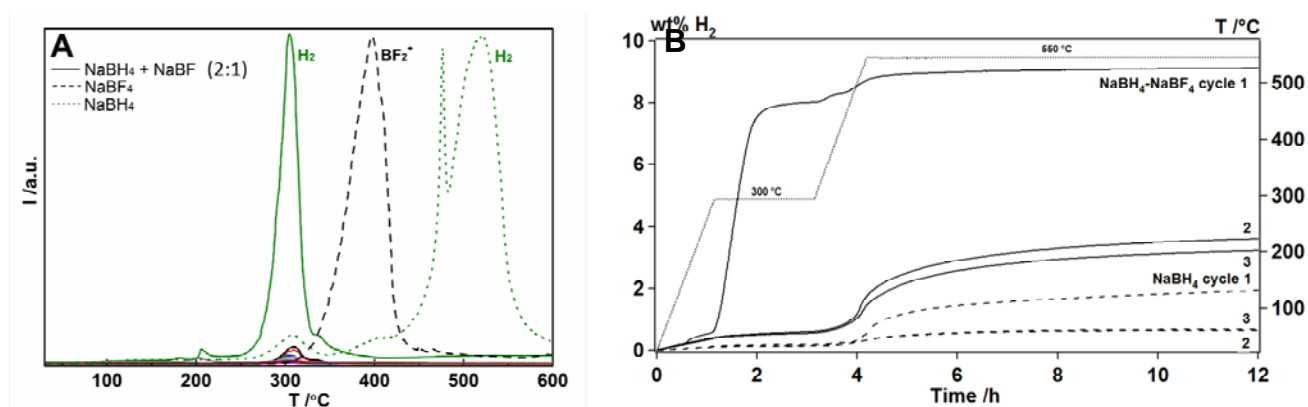


Fig. 6: A) TPD-MS measurement of  $NaBH_4$ - $NaBF_4$  (2:1) compared to reference  $NaBH_4$  and  $NaBF_4$  in the temperature range from RT to 600 °C. B) Sieverts' measurements showing hydrogen desorption cycles 1 to 3 for samples  $NaBH_4$  (R1, see dashed line) and  $NaBH_4$ - $NaBF_4$  (1:0.5, S2, solid line). Hydrogen desorption was performed at fixed temperatures of 300 and 550 °C (heating rate was 4 °C/min; the temperature profile is shown as dots).

### Anion substitution in $LiBH_4$

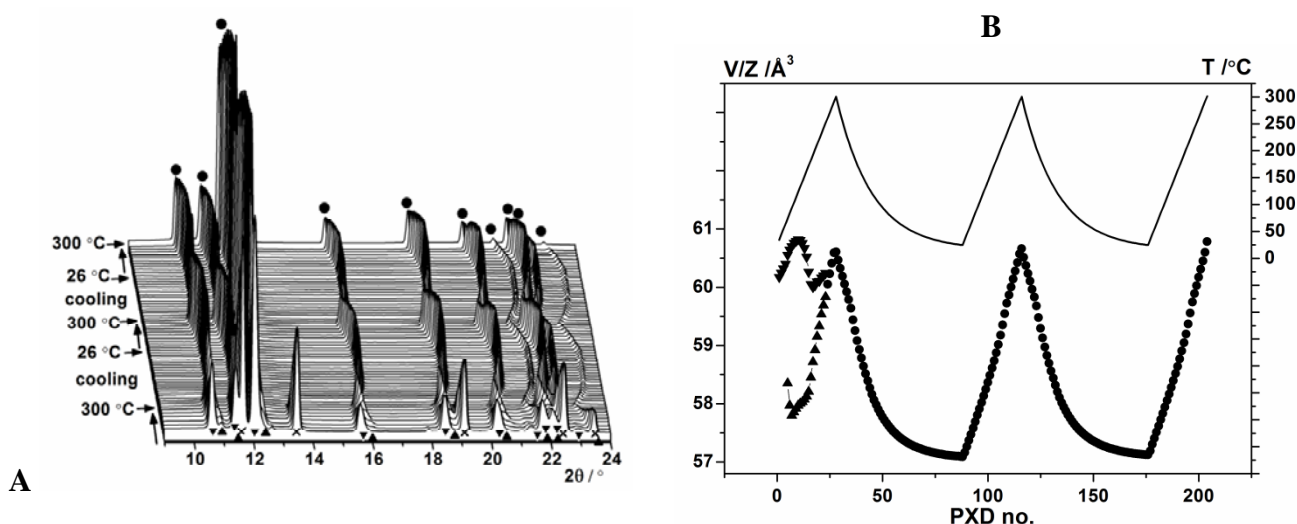


Fig. 7: A) In-situ SR-PXD data ( $\lambda = 0.709637 \text{ \AA}$ ) for a ball-milled sample of  $LiBH_4$ - $LiI$  (1:0.5) measured at ESRF BM01A. The sample was heated from RT to 300 °C and cooled to 26 °C three times (5 °C/min). B) Unit cell volumes per formula unit  $V/Z$  for the two solid solutions  $h-Li(BH_4)_{1-x}I_x$  and  $h-Li(BH_4)_{1-y}I_y$  and  $h-Li(BH_4)_{0.61}I_{0.39}$  (ratio determined from Rietveld refinements of the data shown in A) plotted as a function of scan no. (PXD no.), while the temperature was cycled. Notice the formation of two solid solutions at the beginning of the first cycle. Symbols (A): ▼  $h-Li(BH_4)_{1-x}I_x$ , ▲  $h-Li(BH_4)_{1-y}I_y$ , ●  $h-Li(BH_4)_{0.61}I_{0.39}$ . The solid line in (B) shows the corresponding temperature.

Anion substitution of Cl, Br and I readily occurs in lithium borohydride, resulting in stabilization of the metal borohydride. For the  $LiBH_4$ - $LiI$  system anion substitution is observed as formation of two solid solutions of  $Li(BH_4)_{1-x}I_x$ , which merge into a single solution upon heating (Fig. 7). The solid solutions have hexagonal structures (space group  $P6_3mc$ ) similar to the structures of  $h-LiBH_4$  and  $\beta$ -

<sup>1</sup> Ref: L. H. Rude, U. Filsøe, S. Hino, O. Zavorotynska, M. Baricco, B. Hauback, F. Besenbacher, J. Skibsted, T. R. Jensen, ( $NaBH_4$ - $NaBF_4$ ) (to be submitted 2012)

LiI. The solid solutions have iodide contents in the range ~0 to ~62 mol% and are stable from below room temperature to the melting point at 330 °C. Thus the stability of the solid solutions is higher than that of the orthorhombic and hexagonal polymorphs of LiBH<sub>4</sub>, as well as  $\alpha$ - and  $\beta$ -LiI. Furthermore, the rehydrogenation properties of the iodide substituted solid solution Li(BH<sub>4</sub>)<sub>1-x</sub>I<sub>x</sub>, measured by the Sieverts method, are slightly improved as compared to those of LiBH<sub>4</sub>. After four cycles of hydrogen release and uptake the Li(BH<sub>4</sub>)<sub>1-x</sub>I<sub>x</sub> solid solution maintains 68% of the calculated hydrogen storage capacity in contrast to LiBH<sub>4</sub>, which maintains only 25% of the storage capacity after two cycles under identical conditions.

### Cl and Br substitution in Mg(BH<sub>4</sub>)<sub>2</sub>

Substitution of Cl and Br for BH<sub>4</sub><sup>-</sup> is observed in Mg(BH<sub>4</sub>)<sub>2</sub> when ball-milled mixtures of Mg(BH<sub>4</sub>)<sub>2</sub> + MgX<sub>2</sub> (X = Cl and Br) are annealed at 200°C, which is right above the  $\alpha$ -to- $\beta$  transition temperature. The  $\beta$ -modification of Mg(BH<sub>4</sub>)<sub>2</sub> is preserved upon cooling to ambient temperature. High-resolution SR-PXD reveals a significant contraction of the unit cell, which is ascribed to the substitution of BH<sub>4</sub><sup>-</sup> by the smaller halides (Fig. 8). The halide substitution has a small destabilizing effect as hydrogen release occurs at about 30°C lower temperature than for pure Mg(BH<sub>4</sub>)<sub>2</sub>.

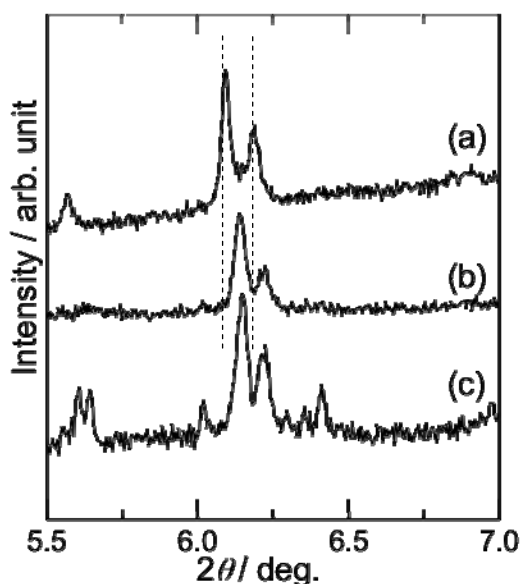


Fig. 8: SR-PXD ( $\lambda = 0.50123 \text{ \AA}$ ) profile for (a) the sample after heating of pure Mg(BH<sub>4</sub>)<sub>2</sub> up to 300 °C, (b) Mg(BH<sub>4</sub>)<sub>2</sub> + MgBr<sub>2</sub> and (c) Mg(BH<sub>4</sub>)<sub>2</sub> + MgCl<sub>2</sub> milled for 12 h at 280 rpm and annealed for 10 h at 200 °C. The measurements were performed at room temperature. The dashed lines are to guide the eye for the shifts in the peak positions for  $\beta$ -Mg(BH<sub>4</sub>)<sub>2</sub>.

### The Cl substitution in Ca(BH<sub>4</sub>)<sub>2</sub>

The  $\alpha$ -phase is the most prominent Ca(BH<sub>4</sub>)<sub>2</sub> modification after ball milling Ca(BH<sub>4</sub>)<sub>2</sub>–CaCl<sub>2</sub> in the molar ratio 1:1. Calcium chloride is present as two modifications with space groups Pnnm and Pbcn, the latter being metastable. The formation of the Pbcn modification may be triggered by the presence of Ca(BH<sub>4</sub>)<sub>2</sub> or by the milling process. Quantitative phase analysis by Rietveld refinement gave a phase composition of close to the nominal 1:1 ratio. The refined unit cell parameters for  $\alpha$ -Ca(BH<sub>4</sub>)<sub>2</sub> were  $a = 7.44 \text{ \AA}$ ,  $b = 13.13 \text{ \AA}$ ,  $c = 8.79 \text{ \AA}$ , which is similar to the literature values. Thus, no chloride substitution occurs during BM.

The phase evolution at elevated temperatures was investigated by *in-situ* SR-PXD (Fig. 9). Upon heating,  $\alpha$ -Ca(BH<sub>4</sub>)<sub>2</sub> transformed into  $\beta$ -Ca(BH<sub>4</sub>)<sub>2</sub> in the temperature interval from 150 to 200 °C. At about 260 °C, shoulders appear on the high-angle side of the  $\beta$ -Ca(BH<sub>4</sub>)<sub>2</sub> peaks, indicating formation of a phase with similar crystal structure but smaller unit cell volume, i.e. substitution of BH<sub>4</sub><sup>-</sup> with the smaller Cl<sup>-</sup> ion.

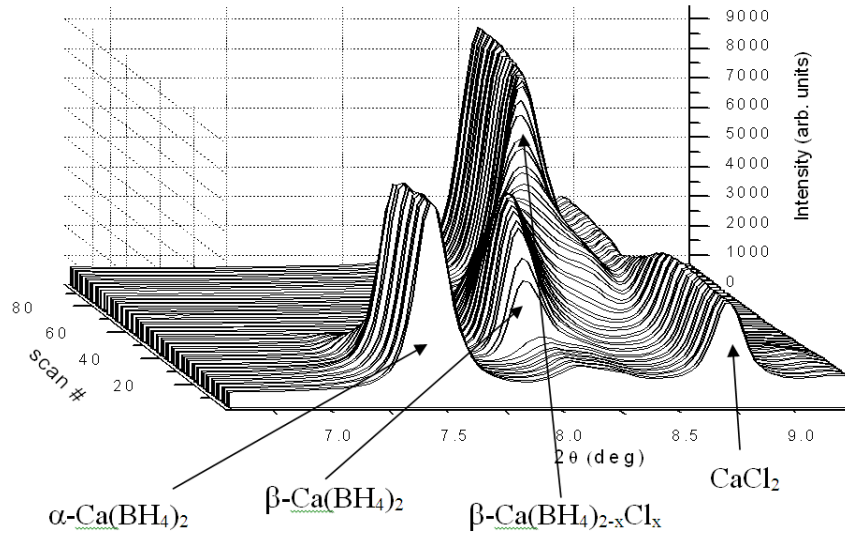
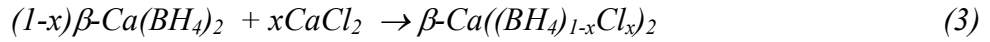


Fig. 9: In-situ SR-PXD data of  $\text{Ca}(\text{BH}_4)_2 + \text{CaCl}_2$  upon heating. Evolution of a  $\text{Ca}((\text{BH}_4)_{1-x}\text{Cl}_x)_2$  phase is evident from around  $260^\circ\text{C}$ .



Upon further heating,  $\beta\text{-Ca}(\text{BH}_4)_2$  completely transforms into the chlorine substituted phase. Rietveld refinement reveal a solid solution with composition,  $\beta\text{-Ca}((\text{BH}_4)_{0.6}\text{Cl}_{0.4})_2$ .

$\text{CaBr}_2$  ( $V = 196 \text{ \AA}^3$ ) and  $\text{CaCl}_2$  ( $V = 168 \text{ \AA}^3$ ) are isostructural (space group  $Pnm\bar{m}$ ). However,  $\text{CaBr}_2$  behaves markedly different as compared to  $\text{CaCl}_2$  when mixed with  $\text{Ca}(\text{BH}_4)_2$ . No significant change in unit cell volume apart from thermal expansion of  $\text{Ca}(\text{BH}_4)_2$  is observed. Thus, there are no experimental indications of Br- substitution in  $\text{Ca}(\text{BH}_4)_2$ .

#### The $\text{Ca}(\text{BH}_4)_2\text{-CaI}_2$ system

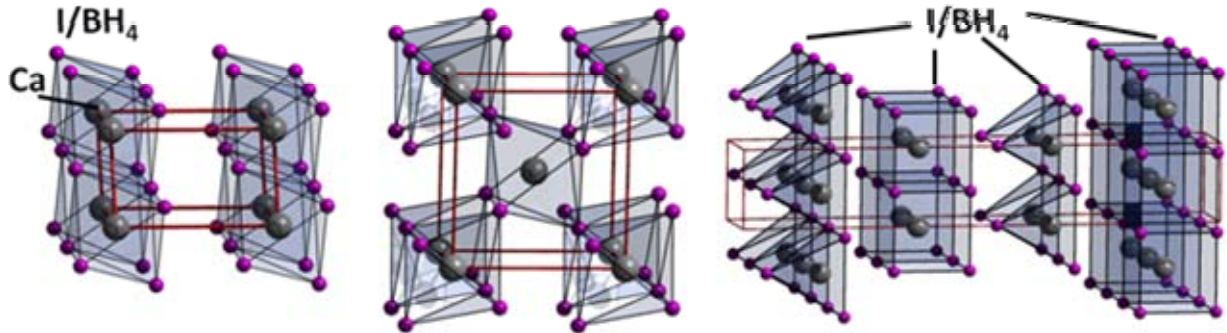


Fig. 10: Crystal structure of the three new compounds found in the  $\text{Ca}(\text{BH}_4)_2\text{-CaI}_2$  system, from left: a  $\text{CaI}_2$ -type trigonal structure  $\text{tri-Ca}((\text{BH}_4)_{0.70}\text{I}_{0.30})_2$  ( $T = 28^\circ\text{C}$ ), a  $\text{CaCl}_2$ -type orthorhombic structure,  $\text{ort-Ca}((\text{BH}_4)_{0.64}\text{I}_{0.36})_2$  ( $T = 310^\circ\text{C}$ ) and a new structure type tetragonal,  $\text{tet-Ca}((\text{BH}_4)_{0.38}\text{I}_{0.62})_2$  with spacegroup  $I4mm$  and cell parameters  $a = 4.110$  and  $c = 24.845 \text{ \AA}$  ( $T = 340^\circ\text{C}$ ). The calcium atoms are shown in grey and I and  $\text{BH}_4^-$ , obtaining the same positions, are shown as purple spheres. The structures were elucidated using Rietveld refinement of in situ-synchrotron radiation powder X-ray diffraction

Three new compounds were identified in the  $\text{Ca}(\text{BH}_4)_2\text{-CaI}_2$  system and structurally characterised using the Rietveld method and SR-PXD data (Fig. 10). Calcium borohydride readily dissolves in the trigonal calcium iodide structure during ball milling, forming a solid solution  $\text{Ca}((\text{BH}_4)_{1-x}\text{I}_x)_2$  with a  $\text{CaI}_2$ -type structure and an anisotropically contracted trigonal unit cell. All three novel compounds found in the  $\text{Ca}(\text{BH}_4)_2\text{-CaI}_2$  system are stable at  $RT$ . The anion substitution ultimately changes the

decomposition reaction pathway in which hydrogen is released from a tetragonal  $\text{Ca}((\text{BH}_4)_{1-x}\text{I}_x)_2$  and via  $\text{CaHI}$ , but unfortunately the temperature of hydrogen release is still fairly high and similar to that for  $\text{Ca}(\text{BH}_4)_2$ .

### Halogen substituted hydrides based on unstable borohydrides

#### Solid state synthesis of $\text{Al}(\text{BH}_4)_3$ and $\text{Zr}(\text{BH}_4)_4$

The unstable borohydride systems  $\text{Al}(\text{BH}_4)_3$  and  $\text{Zr}(\text{BH}_4)_4$  could be synthesized from  $\text{AlCl}_3$  or  $\text{ZrCl}_4$  mixed with stable borohydrides  $\text{LiBH}_4$ ,  $\text{NaBH}_4$ ,  $\text{Ca}(\text{BH}_4)_2$  or  $\text{Mg}(\text{BH}_4)_2$  via a metathesis reaction.

The initial characterization generally showed lower decomposition temperatures compared to the pure metal borohydride material. A very large weight loss was often observed, indicating that other gases than  $\text{H}_2$  were released (Fig. 11). Complex two- and three-step decomposition pathways were observed.

#### $\text{Zr}(\text{BH}_4)_4$ structure, solved from single crystal X-ray data

Single crystal  $\text{Zr}(\text{BH}_4)_4$  was obtained by crystal growth using vapour deposition techniques. The structure of  $\text{Zr}(\text{BH}_4)_4$  was thus solved from single crystal X-ray diffraction and the atomic coordinates determined for the first time including all hydrogen positions.  $\text{Zr}(\text{BH}_4)_4$  is isostructural to  $\text{Hf}(\text{BH}_4)_4$  and crystallizes in a cubic unit cell of space group  $P-43m$  with unit cell parameter  $a = 4.8387(4) \text{ \AA}$  ( $T = 100 \text{ K}$ ). The atoms are occupying the same Wyckoff sites as found for  $\text{Hf}(\text{BH}_4)_4$ , where the transition metal is the only atom occupying a general position.

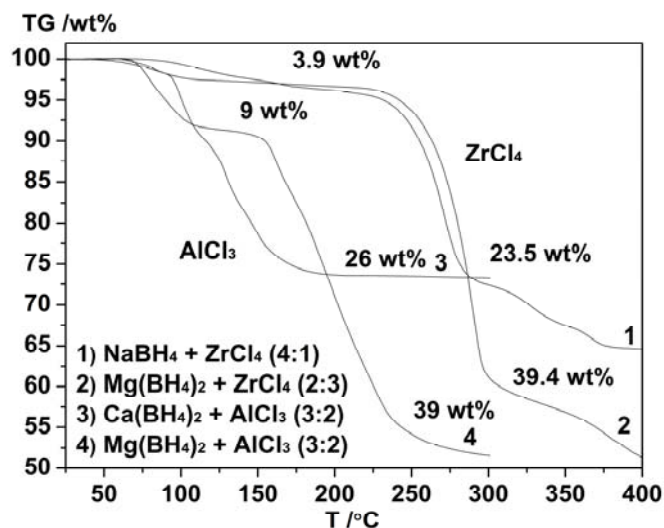


Fig. 11: Thermogravimetric analysis TG for a number of samples of the unstable borohydride systems heated from RT to 300, 350 or 400 °C using a heating rate of 10 °C/min. It is characteristic for these systems that the weightloss is large indicating heavier gasses, e.g.  $\text{B}_2\text{H}_6$  are released. Systems with  $\text{AlCl}_3$  generally decompose at lower temperatures than similar systems with  $\text{ZrCl}_4$ .

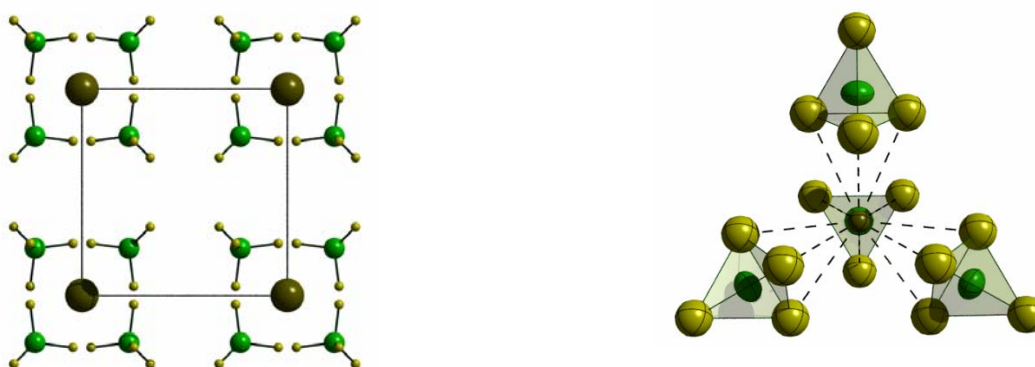


Fig. 12: The cubic crystal structure of  $\text{Zr}(\text{BH}_4)_4$  ( $Z = 1$ ). Zr is shown as army-green spheres and  $\text{BH}_4$  is shown as dark and light green spheres. In the upper right corner, anisotropic displacement ellipsoids of the tetrahedral coordination of Zr to the faces of four  $\text{BH}_4$  tetrahedra are shown.

The anion-anion distances are  $3.7752(17) \text{ \AA}$  and cation-anion distances are  $2.3118(12) \text{ \AA}$  for  $\text{Zr}(\text{BH}_4)_4$ , in both cases slightly larger than those observed in  $\text{Hf}(\text{BH}_4)_4$ . However, the Zr-H and B-H distances in  $\text{Zr}(\text{BH}_4)_4$  are slightly shorter than those found in  $\text{Hf}(\text{BH}_4)_4$ . The distances and angles for the  $\text{BH}_4^-$



anions reveal that the distortion of the tetrahedral shape is slightly larger for  $\text{Zr}(\text{BH}_4)_4$  than for  $\text{Hf}(\text{BH}_4)_4$ .

### Halogen substituted hydrides based on Reactive Hydride Composites (RHC)

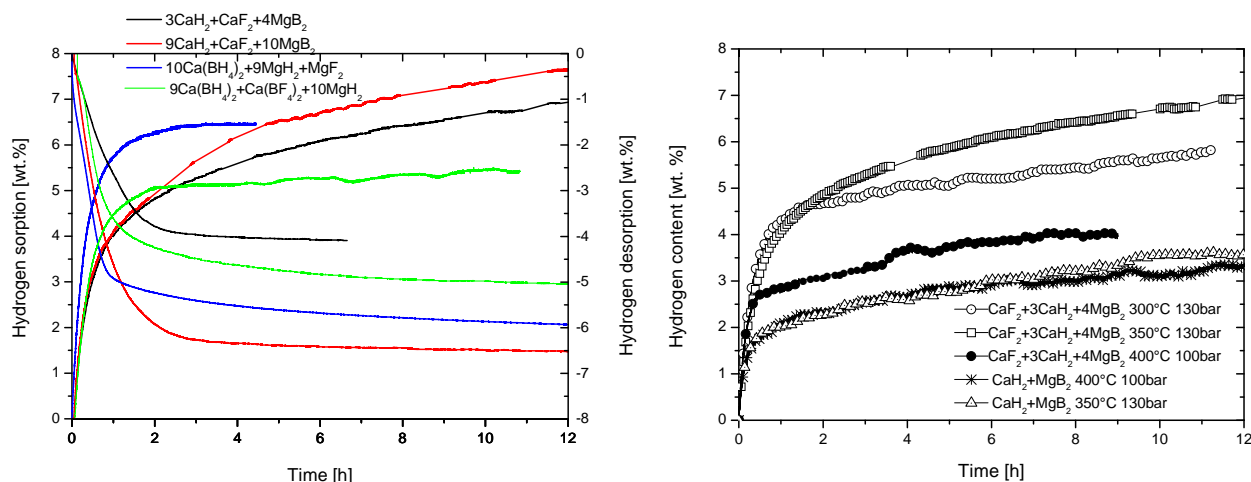


Fig. 13: Kinetics curves of the Ca-based reactive hydride composites.

left: first hydrogenation cycle at 130bar and 350° of fluorinated  $\text{CaH}_2/\text{MgB}_2$  systems

right: hydrogenation behaviour of non-fluorinated and fluorinated  $\text{CaH}_2/\text{MgB}_2$  systems at different temperatures and pressures

Various Ca-based RHC samples with  $\text{CaF}_2$  as the source of F were prepared by ball milling in an argon filled glove box. The first purpose of these different compositions was to identify a good balance between the expected improvement in thermodynamics and the decrease in the hydrogen storage capacity by substituting fluorine for hydrogen. The second purpose was to identify the influence of the fluorine source on the reactivity of the system. For comparison the composite  $\text{CaH}_2+\text{MgB}_2$  was also prepared and tested.

Fig. 13 left presents the behaviour during the first hydrogenation cycle at 130bar and 350°C of samples with varying F content, prepared from Calcium Fluoride and Hydride and Magnesium Diboride, according to the composition  $x\text{CaF}_2+y\text{CaH}_2+z\text{MgB}_2$ , and also from Calcium Borohydride and Calcium Borofluoride. For comparison Fig. 13 right presents the hydrogenation behaviour of non-fluorinated and fluorinated  $\text{CaH}_2/\text{MgB}_2$  systems at different temperatures and pressures. It is important to notice that the incorporation of fluorine (with exception of the  $9\text{Ca}(\text{BH}_4)_2+\text{Ca}(\text{BF}_4)+10\text{MgH}_2$  sample) does not reduce drastically the theoretical hydrogen storage capacity, meeting the objective of keeping the hydrogen storage capacity higher than 6 wt%. Compared to the reference  $\text{CaH}_2+\text{MgB}_2$  RHC (Fig. 13 right), under the same testing conditions the hydrogen absorption rate is doubled, proving the positive effect of fluorine presence in the system.

The best results in hydrogen storage capacity were found in  $\text{CaF}_2 + 3\text{CaH}_2 + 4\text{MgB}_2$  and  $\text{CaF}_2 + 9\text{CaH}_2 + 10\text{MgB}_2$  systems. So during the rest of FLYHY,

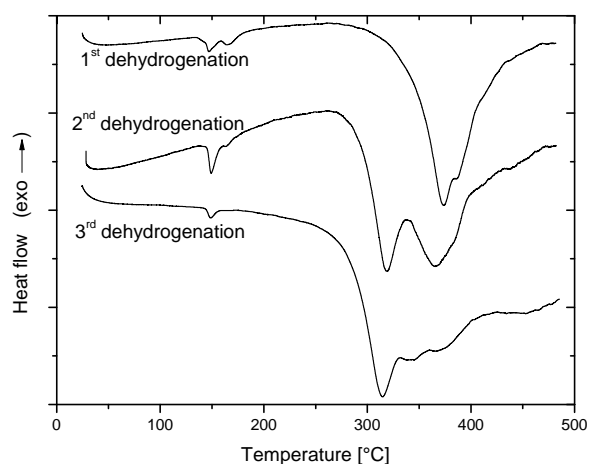


Fig. 14: DSC signal of hydrogenated  $\text{CaF}_2+3\text{CaH}_2+4\text{MgB}_2$  composite, measured at  $5 \text{ K min}^{-1}$  (The hydrogenated samples were heated from room temperature to 500°C with a heating rate of 2, 5 and  $10 \text{ K min}^{-1}$  under an argon flow of  $50 \text{ ml min}^{-1}$ .)

the investigations focused on these compositions.

During the early stage of FLYHY, literature studies and theoretical calculations in WP3 it became clear that many of the relevant fluorides are thermodynamically very stable ionic compounds. In order to design a reversible hydrogen storage system including those fluorides it might be necessary to have stable fluorides both as products and reactants, as e.g. in the RHC systems. This new principle was explored not only in the calcium, but also in lithium and sodium based RHC. But in these systems, except an increase in reaction speeds, no comparable positive effects on kinetics as in the Ca-based RHC could be observed, while retaining most of the hydrogen storage capacity. Therefore investigations in FLYHY mainly focused on the Ca-based RHC with F addition.

The reaction enthalpy for dehydrogenation of the Ca-RHC systems could be estimated using differential scanning calorimetry (DSC). Fig. 14 shows DSC profiles of the  $\text{CaF}_2+3\text{CaH}_2+4\text{MgB}_2$  composite after the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> hydrogenation of the sample. The peak at 148°C can be associated to  $\alpha\text{-Ca}(\text{BH}_4)_2$  to  $\beta\text{-Ca}(\text{BH}_4)_2$  phase transformation. The peak at 165°C may be associated with another phase transformation. In addition, there is a decrease in peak desorption temperature from 360°C in the first cycle to 290 °C ( $2\text{ K min}^{-1}$ ). The onset desorption temperature decreases from 300°C to ca. 250°C ( $2\text{ K min}^{-1}$ ) from the first to the third cycle; i.e. an improvement in the reaction thermodynamics. This has to be compared with the pure Ca-based RHC, where Desorption starts at 350°C only. Evaluation of the DSC measurements resulted in an **average dehydrogenation reaction enthalpy of  $48.6 \pm 3.2\text{ kJ}/(\text{mol H}_2)$** . This dehydrogenation enthalpy, being rather high compared to the expectations, can be explained by the fact that the dehydrogenation process is composed of two peaks. The beginning and the end of those peaks are not well defined, and the total area under the curve was used in the calculation of enthalpy changes. The contribution of each peak is not resolved and the dehydrogenation enthalpy change is rather a global one. Similar experiments were performed in the  $\text{CaF}_2+9\text{CaH}_2+10\text{MgB}_2$  system. The average dehydrogenation enthalpy of  $51.5 \pm 2.4\text{ kJ}/(\text{mol H}_2)$  was found for this system. This indicates an increase of the reaction enthalpy with a decrease of F content in the system.

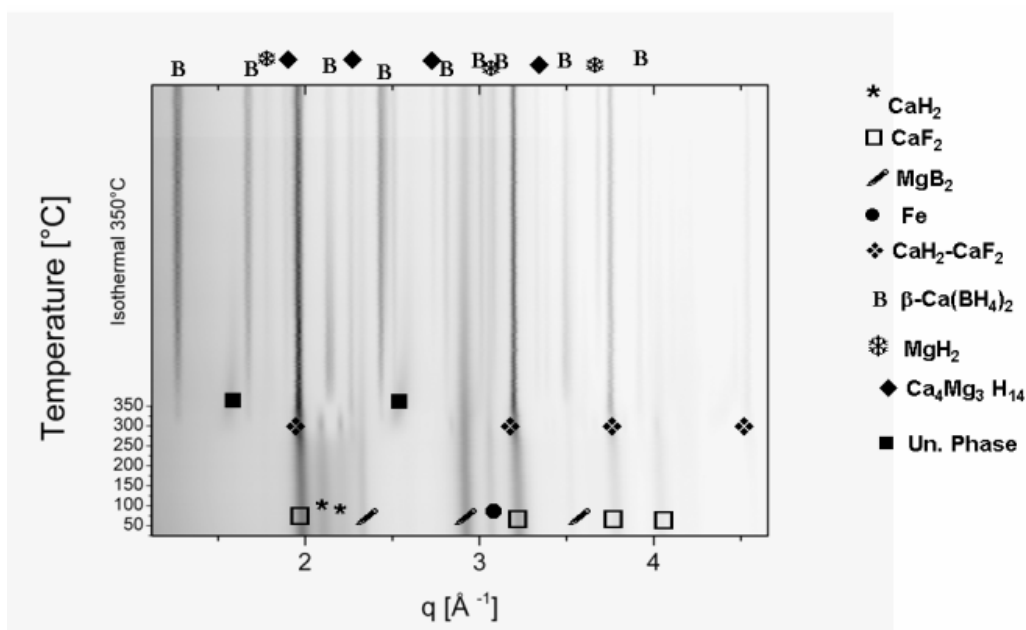


Fig. 15: *In situ* SR-PXD patterns of the as milled  $\text{CaF}_2+3\text{CaH}_2+4\text{MgB}_2$  composite, hydrogenation at 130 bar and heating from room temperature to 350 °C.

Activation energies for the dehydrogenation reaction in the systems  $\text{CaF}_2+3\text{CaH}_2+4\text{MgB}_2$  and  $\text{CaF}_2+9\text{CaH}_2+10\text{MgB}_2$  were also obtained from DSC experiments via evaluation by the Kissinger method. **The activation energy of the first dehydrogenation reaction decreased from  $E_A = 162 \pm 15\text{ kJ}/(\text{mol H}_2)$  to  $E_A = 116 \pm 5\text{ kJ}/(\text{mol H}_2)$  over 3 hydrogen unloading and loading cycles.** Similar



experiments were performed in the **CaF<sub>2</sub>+9CaH<sub>2</sub>+10MgB<sub>2</sub>** system, yielding values of  $E_A = 173 \pm 16$  /(mol H<sub>2</sub>) and  $E_A = 121 \pm 9$  kJ/(mol H<sub>2</sub>), respectively. There is a consistent increase in the measured values with a decrease in the F content in the system showing a beneficial effect of F on sorption kinetics.

In order to clarify the reaction path during hydrogenation, the hydrogen absorption reaction of the system CaF<sub>2</sub> + 3CaH<sub>2</sub> + 4MgB<sub>2</sub> was investigated by means of the *in situ* synchrotron radiation powder X-ray diffraction technique (Fig. 15). The phases present in the starting material are CaF<sub>2</sub>, CaH<sub>2</sub> and MgB<sub>2</sub> plus an amount of residual iron from ball milling of about 1 wt.%.

At 270 °C a solid solution between CaH<sub>2</sub> and CaF<sub>2</sub> is formed, as at this temperature CaH<sub>2</sub> though being thermodynamically stable is highly soluble in CaF<sub>2</sub>. Simultaneously to the CaH<sub>2</sub> disappearance and the intensity raise of the CaF<sub>2</sub> peaks, the formation of β-Ca(BH<sub>4</sub>)<sub>2</sub> and the appearance of two unidentified signals at 1.56 Å<sup>-1</sup> and 2.55 Å<sup>-1</sup> is observed. Once the CaF<sub>2</sub>-CaH<sub>2</sub> solid solution is formed, it acts as the only Ca-source for the formation of Ca(BH<sub>4</sub>)<sub>2</sub> in the system. The formation of β-Ca(BH<sub>4</sub>)<sub>2</sub> is followed at 280 °C by the formation of Ca<sub>4</sub>Mg<sub>3</sub>H<sub>14</sub> and MgH<sub>2</sub>. During the isothermal period at 350 °C, together with the intensity rising of β-Ca(BH<sub>4</sub>)<sub>2</sub>, Ca<sub>4</sub>Mg<sub>3</sub>H<sub>14</sub> and MgH<sub>2</sub>, a decrement of the peaks of the CaF<sub>2</sub>-CaH<sub>2</sub> solid solution and the complete disappearance of the signals at 1.56 Å<sup>-1</sup> and 2.55 Å<sup>-1</sup> are observed.

Due to the possible formation of amorphous compounds, samples from HZG were characterized by the <sup>11</sup>B MAS NMR technique at AU. It was found, that in the as milled samples unreacted MgB<sub>2</sub> is present as in the MgB<sub>2</sub> reference (Fig. 16 a) and b)). After hydrogenation Ca(BH<sub>4</sub>)<sub>2</sub> is formed, the MgB<sub>2</sub> content is decreased strongly (Fig. 16 c). After 5 dehydrogenation / hydrogenation cycles the Ca(BH<sub>4</sub>)<sub>2</sub> content is decreased significantly compared to the 1<sup>st</sup> cycle and amorphous boron as well as CaB<sub>12</sub>H<sub>12</sub> (at -14 ppm) are formed. As reported in literature the CaB<sub>12</sub>H<sub>12</sub> and amorphous boron are stable products of the decomposition of Ca(BH<sub>4</sub>)<sub>2</sub>, and not participating in the hydrogenation reaction any more. Besides the observed formation of Ca<sub>4</sub>Mg<sub>3</sub>H<sub>14</sub> compound, these findings explain the observed decrease and then stability of hydrogen storage capacity (Fig. 30, page - 25 -.

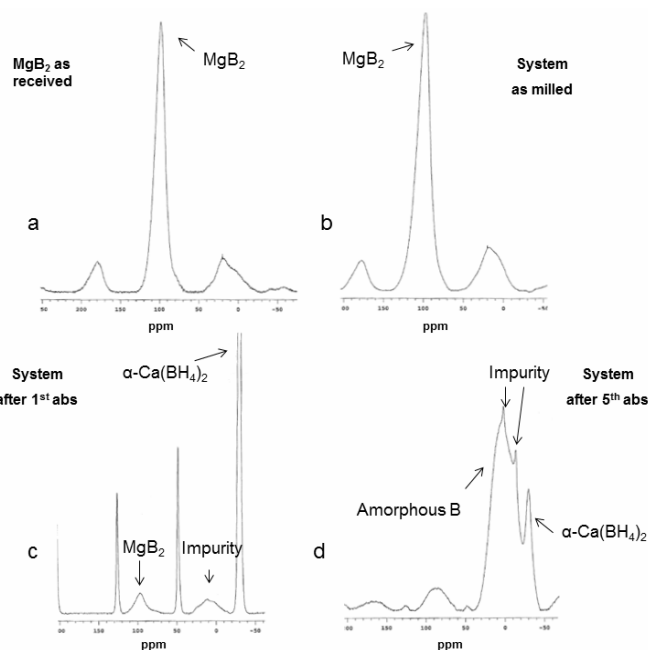


Fig. 16: <sup>11</sup>B MAS NMR analysis of the CaF<sub>2</sub> + 3CaH<sub>2</sub> + 4MgB<sub>2</sub> system: a) material as received, b) material as milled, c) material after first absorption, d) material after fifth absorption.

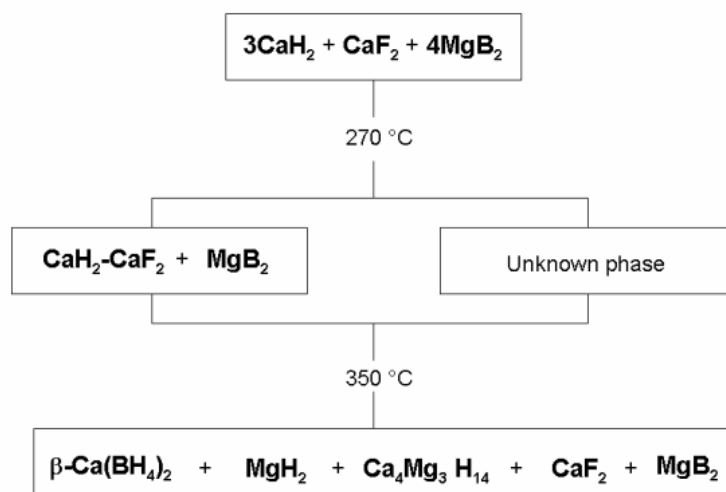
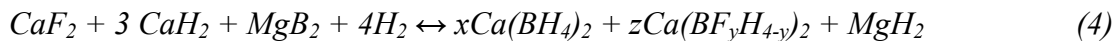


Fig. 17: Hydrogen absorption reaction scheme of the system 3CaH<sub>2</sub>+4MgB<sub>2</sub>+CaF<sub>2</sub>.

The absorption reaction mechanism of the  $\text{CaF}_2 + 3\text{CaH}_2 + 4\text{MgB}_2$  system can be summarised by the scheme in Fig. 17.

Besides the formation of the  $\text{CaH}_2$ - $\text{CaF}_2$  solid solution upon heating of the samples (the formation of this solution could not be obtained by ball milling at room temperature alone), it was unclear, whether the intended substitution of F for H in the  $\text{Ca}(\text{BH}_4)_2$  hydrogenation product takes place.

In order to obtain more detailed structural information of the Boron surroundings, the suggested reaction



was studied by NEXAFS at the boron K-edge. Both the hydrogenated state (ab), which corresponds to the right side of reaction 4, and the dehydrogenated state (de), which corresponds to the left side of 4, were studied. NEXAFS results suggest a tendency of dehydrogenated states to present boron trigonal plane structures. There is a clear peak shift position of the fluorine substituted RHC with respect to  $\text{Ca}(\text{BH}_4)_2$  (Fig. 18). It indicates a *change in the B neighbourhood and the formation of different bonds, producing a more electronegative ambient* that shifts the peak position, thus indicating, that indeed F substitutes for H in the  $\text{BH}_4^-$  groups of the Ca-based RHC.

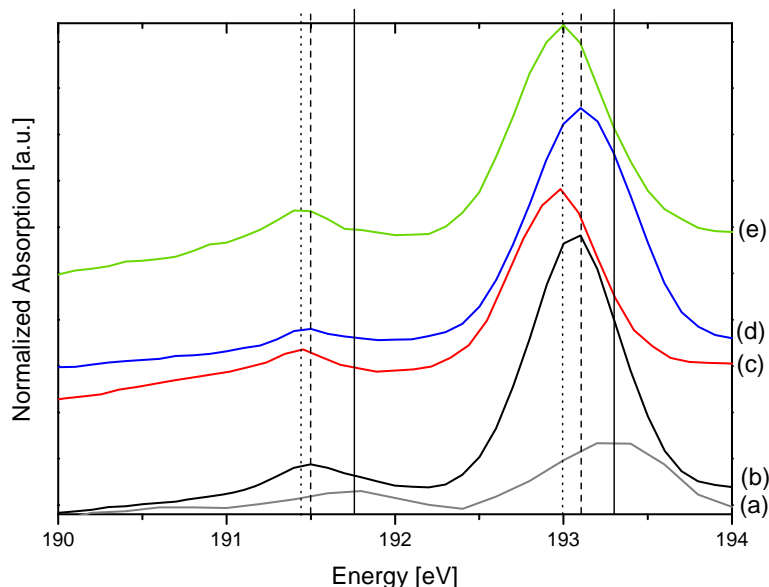


Fig. 18: Detail of B K-edge NEXAFS spectra of (a)  $\text{Ca}(\text{BH}_4)_2$  dry from  $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ , (b)  $\text{CaF}_2 + 3 \text{CaH}_2 + \text{MgB}_2$  1ab, (c)  $\text{CaF}_2 + 3 \text{CaH}_2 + \text{MgB}_2$  1de, (d)  $\text{CaF}_2 + 3 \text{CaH}_2 + \text{MgB}_2$  2ab, (e)  $\text{CaF}_2 + 3 \text{CaH}_2 + \text{MgB}_2$  2de.

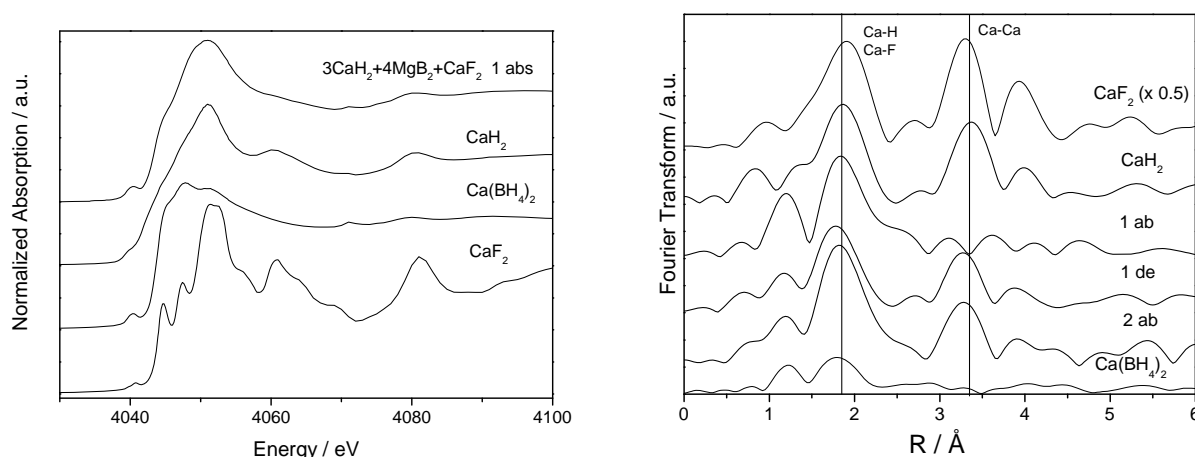


Fig. 19: XANES spectra at the Ca K-edge (left) and Fourier transform of the EXAFS signals at the Ca K-edge of  $\text{CaF}_2$ ,  $\text{CaH}_2$ ,  $\text{Ca}(\text{BH}_4)_2$  and  $3\text{CaH}_2 + 4\text{MgB}_2 + \text{CaF}_2$  after the 1<sup>st</sup> hydrogenation (1 ab), after the 1<sup>st</sup> dehydrogenation, (1 de) and after the 2<sup>nd</sup> hydrogenation (2 ab) (right).

Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) and XANES experiments at the Ca K-edge were performed at the A1 beamline of the DESY synchrotron, Hamburg, Germany, and at the

XAFS2 beamline of the Laboratorio Nacional de Luz Sincrotron (LNLS), Campinas, Brazil. Fig. 19 shows the XANES and EXAFS spectra at the Ca K-edge of  $\text{CaF}_2$ ,  $\text{CaH}_2$ ,  $\text{Ca}(\text{BH}_4)_2$ ,  $\text{Ca}(\text{BF}_4)_2$ , and  $3\text{CaH}_2+4\text{MgB}_2+\text{CaF}_2$  after the different hydrogenation cycles. The XANES spectrum of  $3\text{CaH}_2+4\text{MgB}_2+\text{CaF}_2$  after the 1<sup>st</sup> hydrogenation can be described mainly as a linear combination of  $\text{Ca}(\text{BH}_4)_2$ ,  $\text{CaF}_2$  and minor part of  $\text{Ca}(\text{BF}_4)_2$ . It gives no conclusive evidence for the intended F substitution.

Regarding the EXAFS results, they suggest the presence of fluorine atoms in the first coordination shells of Ca, but not in a  $\text{CaF}_2$  structure, as the Ca-Ca peak at 3.3 Å is not present. However,  $\text{Ca}(\text{BF}_4)_2$  was not formed according to XANES results at the B K-edge, so a different compound should be present.

This result is consistent with the formation of a  $\text{CaH}_2$ - $\text{CaF}_2$  solid solution observed in the *in situ* SR-PXD (Fig. 15). After the desorption process, the Fourier Transform of the EXAFS signal resembles that of the  $\text{CaH}_2$ , including the appearance of the Ca-Ca coordination shell at 3.3 Å. Thus,  $\text{CaH}_2$ ,  $\text{CaF}_2$  or even a  $\text{CaH}_{2-x}\text{F}_x$  solid solution could be present, as confirmed by *in situ* SR-PXD (Fig. 15). After the second absorption cycle, the peak at 3.3 Å remains almost unaltered indicating that this cycle is proceeding through a different pathway than the first one, which again is consistent with the reaction scheme shown in Fig. 17.

## Main scientific results

### F substitution in alane

- As supported by theoretical calculations in FLYHY on the immiscibility of F in alane, no F substitution could be obtained in alane.

### New route for synthesis of halogen free $\alpha$ - $\text{Ca}(\text{BH}_4)_2$

- A new method for synthesis of  $\text{Ca}(\text{BH}_4)_2$  with very high elemental- and phase purity was developed by Aarhus University, and is currently being patented

### Determination of enthalpy and entropy for pure $\text{Ca}(\text{BH}_4)_2$ synthesized at University of Aarhus

- Pure  $\alpha$ - $\text{Ca}(\text{BH}_4)_2$  synthesized in order to determine precise values for enthalpy and entropy of dehydrogenation of  $\text{Ca}(\text{BH}_4)_2$ . Method is being patented by Aarhus University.

### Significant destabilization of metal borohydrides by addition of metal tetrafluoroborates (Li, Na, Ca)

- Mixtures of metal borohydrides and metal tetrafluoroborates result in strong destabilization of the borohydride part and in release of gaseous mixtures.

### Fluorine substitution observed/indicated using *in situ*-SR-PXD and Rietveld refinement methods.

- In situ*-SR-PXD experiments on mixtures of  $\text{LiBH}_4$  and  $\text{LiBF}_4$  have been analysed using Rietveld refinement, and preliminary results indicate the presence of direct fluorine substitution in  $\text{LiBH}_4$  at elevated temperatures.

### Improved hydrogen cyclability for $\text{NaBH}_4$ - $\text{NaBF}_4$ mixtures

- $\text{NaBH}_4$ - $\text{NaBF}_4$  mixtures desorb mainly hydrogen and have been shown to possess enhanced hydrogen cyclability capabilities. Moreover the temperature of desorption has been decreased by almost 50%.

### Anion substitution in $\text{LiBH}_4$

- The larger halides easily substitute into the lattice of  $\text{LiBH}_4$  forming solid solutions with tuned properties of dehydrogenation. The rehydrogenation properties are slightly improved with respect to the hydrogen capacity left after a dehydrogenation-rehydrogenation cycle.

### The $\text{Ca}(\text{BH}_4)_2\text{-CaI}_2$ system

- As observed for  $\text{LiBH}_4$ ,  $\text{Ca}(\text{BH}_4)_2$  forms solid solutions with the larger halides, and in the case of  $\text{CaI}_2$  three new structures have been discovered and their crystallographic structures solved. The decomposition pathway has changed, but the temperature of decomposition has barely moved.

### $\text{Zr}(\text{BH}_4)_4$ structure, solved from single crystal X-ray data

- By employing vapour deposition techniques, after ball milling  $\text{ZrCl}_4$  and  $\text{LiBH}_4$ , single crystals of  $\text{Zr}(\text{BH}_4)_2$  were collected and examined by single crystal X-ray diffraction experiments. The structure of an unstable borohydride material including all hydrogen positions could thus be solved for the first time.

### Ca-based RHC

- The hydrogenation and dehydrogenation reactions of composites  $\text{CaF}_2 + x\text{CaH}_2 + y\text{MgB}_2$  were demonstrated. A slight decrease of dehydrogenation enthalpy and activation energy of dehydrogenation with an increase in the F content in the system was found. A reduction in the dehydrogenation activation energy, from  $162 \pm 15$  kJ/mol to  $116 \pm 5$  kJ/mol, within 3 cycles was observed, indicating a consistent increase in the measured values with a decrease in the F content in the system. The reaction enthalpy was estimated from DSC measurements as 49 kJ/(mol  $\text{H}_2$ ) in the  $\text{CaF}_2 + 3\text{CaH}_2 + 4\text{MgB}_2$  system. Upon cycling, there is a reduction in the dehydrogenation temperature of the material. In the third cycle, the onset of hydrogen desorption was decreased to ca. 250°C; ca. 100°C lower than in the pure  $\text{CaH}_2 + \text{MgB}_2$  composite without Fluorine.
- Twin peaks observed in DSC profiles and *in-situ* SR-PXD as well as NEXAFS and XANES data hint to the substitution of F for H atoms in  $\text{Ca}(\text{BH}_4)_2$  structures in composites with higher F contents ( $\text{CaF}_2 + 3\text{CaH}_2 + 4\text{MgB}_2 + 14\text{H}_2$ , 3.6 atomic % F). In contrast, IR spectra showed no indication of fluorine substitution.
- Cr and Ni were found (by XANES and NEXAFS) being the most efficient additives to promote fluorination of  $\text{Ca}(\text{BH}_4)_2$  in  $\text{CaF}_2 + 3\text{CaH}_2 + 4\text{MgB}_2$  RHC.

### Li-based RHC

- Chemical interaction between  $\text{LiF}$ ,  $\text{MgB}_2$  and  $\text{H}_2$  essentially results in formation of  $\text{LiBH}_4$  and  $\text{MgF}_2$  during hydrogen absorption. Experiments and also theoretical considerations brought no evidence for F substitution in  $\text{BH}_4^-$  groups in the hydrogenated  $\text{LiF} + \text{MgB}_2$  RHC. Different molar ratios between  $\text{LiF}$  and  $\text{MgB}_2$  (1:1; 2:1; 4:1) change only the kinetics of hydrogen absorption-desorption during cycling and the hydrogen capacity of the compounds, but not the basic mechanisms of the reversible reactions.
- $\text{TiF}_4$  and  $\text{NbF}_5$  additives were found to react with the  $\text{LiH-MgB}_2$  RHC, forming  $\text{LiF}$ . Though they form the thermodynamically highly stable  $\text{LiF}$ , it is found that they promote the hydrogen sorption properties of  $\text{LiH} + \text{MgB}_2$  RHC. This might be due to  $\text{TiB}_2$  formation, acting as nucleation sites for  $\text{MgB}_2$  formation upon dehydrogenation as observed in the non fluorinated  $\text{LiBH}_4\text{-MgH}_2$  RHC.

### Na-based RHC

- The inferior hydrogen uptake of the Na-based RHC with F addition, when compared to the theoretical value, is attributed to the formation of  $\text{NaMgH}_3$ . The reversibility of the system is also compromised by the formation of  $\text{NaMgH}_3$ . The main hydrogenation products are  $\text{NaBH}_4$  and  $\text{NaMgH}_3$ . These two materials are formed in different ranges of temperatures, which open the possibility of selective hydrogenation by careful selection and control of temperature and pressure.

### 4.1.5 Work package 3: Theory and Modelling

#### Objectives of the planned investigations of the work package

Computational techniques have been employed for years in order to (i) predict new structures; (ii) suggest or avoid synthesis routes and (iii) complement experimental investigations, also in the field of research devoted to hydrogen storage. The aim of the computational contribution of WP3 includes the three points mentioned above and is tightly correlated to the experimental findings of WP1 and WP2. The main output of the calculations has dealt with the effect of halide substitution inside the lattice of the different metal hydrides and borohydrides, considering also various polymorphs. By computing the thermodynamic quantities related to the mixing reaction of the hydride with the corresponding fluoride, that is enthalpy, entropy and free energy, information about the stabilization or destabilization of the pure compounds were obtained. Another outcome of the simulation has been the calculated IR and Raman spectra for both pure and mixed structures, that were compared to the experimental ones measured by WP2, allowing for a deeper interpretation and assignment of bands indicating the presence or absence of F in the lattice. Finally, calculations were also run on atomic coordinates determined by WP1-2, to better describe the structural properties of the examined compounds. Calphad methods have been used to obtain a full assessment of thermodynamic properties of mixed systems, to be compared with experimental results obtained in WPs 1 and 2.

All the *ab initio* calculations were run by using the quantum-mechanical periodic CRYSTAL code in its latest 09 version. This computational software has been developed by the theoretical chemistry group of prof. Dovesi at the University of Torino and can be used for systems of any dimensionality, from molecules to crystals, by the application of the Bloch theorem and the description of crystalline orbitals with localized Gaussian functions. In this project, the standard level of calculation was considered in the framework of density functional theory (DFT) with the GGA PBE functional and basis set of double-zeta quality. For those structures which required higher accuracy or presented critical features, other functionals and basis set quality were tested, in order to compare results with different set of computational parameters. For instance, the LDA and the hybrid B3LYP functional forms as well as triple-zeta basis set were adopted. Moreover, the role of dispersion forces has also been taken into account, by means of empirical corrections, that is PBE-D\*.

The unit cell of each structure has been fully optimized, *i.e.* both cell parameters and internal coordinates, so that changes in unit cell volume could be monitored with the increasing substitution of halogens. From the calculation of vibrational frequency at Gamma point in the harmonic approximation enthalpy, entropy and free energy of mixing were obtained, applying mechanical statistic equations. Entropy was considered as subdivided into two terms, configurational and thermal, and was calculated using the approximation for ideal solutions,  $S = -R (x \ln x + (1-x) \ln (1-x))$ , where  $x$  is the molar fraction of the substituent.

A difficult task has been dealing with the simulation of halogen substitution in structures where hydrogen in different positions inside the unit cell could be substituted leading to the same composition. Symmetry criteria were followed whenever possible, to select a limited number of configurations to be computed. Specifically for the fluorine substitutions in borohydrides, a rule called locality principle was hypothesized, stating that when more than one H has to be substituted it is preferred to concentrate the substituents on the same tetrahedron (on the same boron) instead of spreading them on different tetrahedra. This principle has been established and verified for various systems. For computing the enthalpy of mixing, the Boltzmann average of data corresponding to the same composition was considered.

When the enthalpy of mixing ( $_{\text{mix}}\Delta H$ ) was available, an assessment pseudobinary phase diagrams has been carried out with the Calphad method. The introduction of calculated values obtained in WP3 together with experimental results taken from the literature or obtained in WP1 and 2 allowed the determination of thermodynamic properties of various mixed systems. Details on the calculation procedure have been described in the first and second Periodic Activity report. Starting from assessed

free energy values for all the compounds, the driving forces for phase transformation could be calculated and the results can be used for kinetic modelling of hydrogenation and dehydrogenation reactions.

### Task 3.2.: Assessment of binary systems

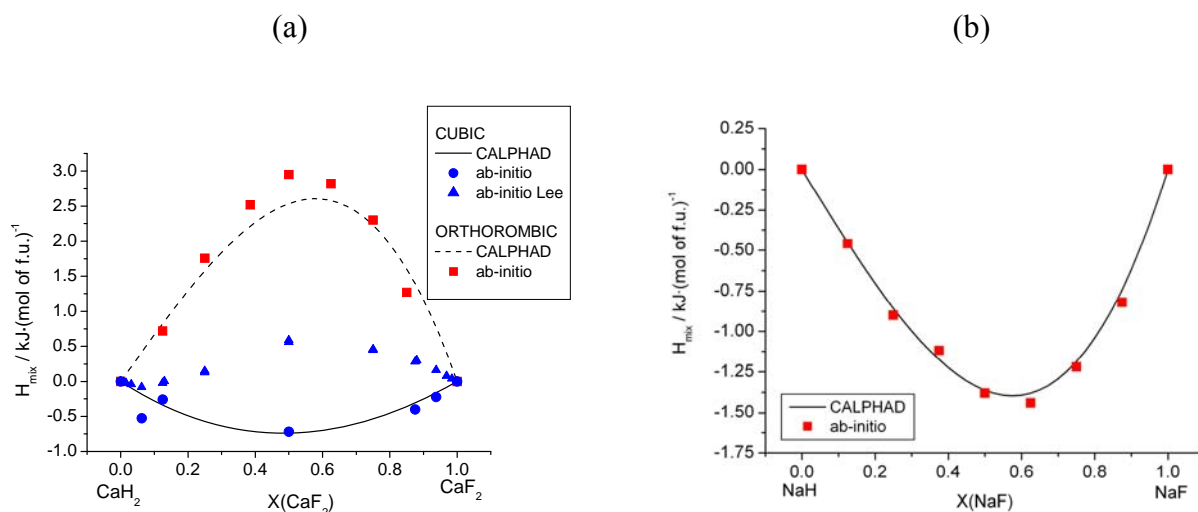


Fig. 20: (a) For  $\text{CaH}_2$  and  $\text{CaF}_2$  ab initio enthalpy of mixing of the orthorhombic (squares) and cubic (circles) solid solutions, the calculations of Lee are also reported for comparison as triangles. The CALPHAD assessed value is represented by the continuous lines; (b) for  $\text{NaH}$  and  $\text{NaF}$  ab initio enthalpy of mixing of the cubic solid solution.

A number of simple metal hydrides were considered for the computational study, namely  $\text{LiH}$ ,  $\text{NaH}$ ,  $\text{CaH}_2$ ,  $\text{MgH}_2$  and  $\text{AlH}_3$ . The two cubic hydrides of lithium and sodium have been modelled with a supercell approach to define a representative unit cell. In the specific case of calcium, the solubility of hydrogen in the corresponding cubic fluoride has also been investigated, adopting a supercell approach as well. The calculated values of enthalpy of mixing were quite large and positive for aluminium hydride and much smaller but still positive for magnesium hydride. While the substitution of fluorine in orthorhombic calcium hydride resulted in a positive  $\text{mix}\Delta H$ , for the substitution of hydrogen in cubic calcium fluoride negative values have been obtained, though in both cases the absolute value is less than 1 kJ/mol per formula unit (as reported in Fig. 20(a)). The calculations performed for F-substitution sodium hydrides (see Fig. 20(b)) have also made on a supercell. In the case of lithium hydride, the calculations have revealed more delicate. In fact, without taking into account dispersion contributions, the enthalpy of mixing resulted negative. On the contrary, calculations including these contributions, performed at the end of the project gave positive values, although always very small, less than 1 kJ/mol per formula unit.

An example of calculated pseudobinary phase diagram is reported in Fig. 21 for the  $\text{CaH}_2$ - $\text{CaF}_2$  system. Due to the entropic contribution and to the low stability of the cubic  $\text{CaH}_2$  with respect to the orthorhombic hydride, a wide range of solubility of H inside the cubic structure of the fluoride was obtained.

Summarizing, for simple metal hydrides, results suggested that the enthalpy of mixing correlates with electronic properties of the base metal. In fact, if the value of the enthalpy of mixing for a constant F substitution of 12.5 % is considered, the values are proportional to Pauling electronegativity (see Fig. 22 left) and to the charge-to-radius values (see Fig. 22 right). It can be concluded that the nature of the M-H chemical bond determines the tendency to F-substitution in the solid state.



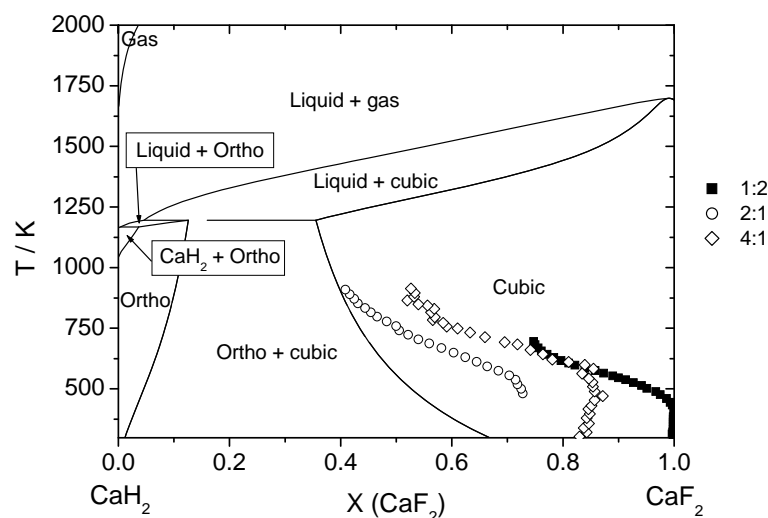


Fig. 21:  $\text{CaH}_2\text{-CaF}_2$  pseudo-binary phase diagram calculated for  $P=1$  bar. The F/H ratio in the cubic structure experimentally observed with XRD (WP2) heating a previously ball milled mixture of  $\text{CaH}_2$  and  $\text{CaF}_2$  with a ratio 1:2 (■), 2:1 (○) and 4:1 (◇) is also reported for comparison.

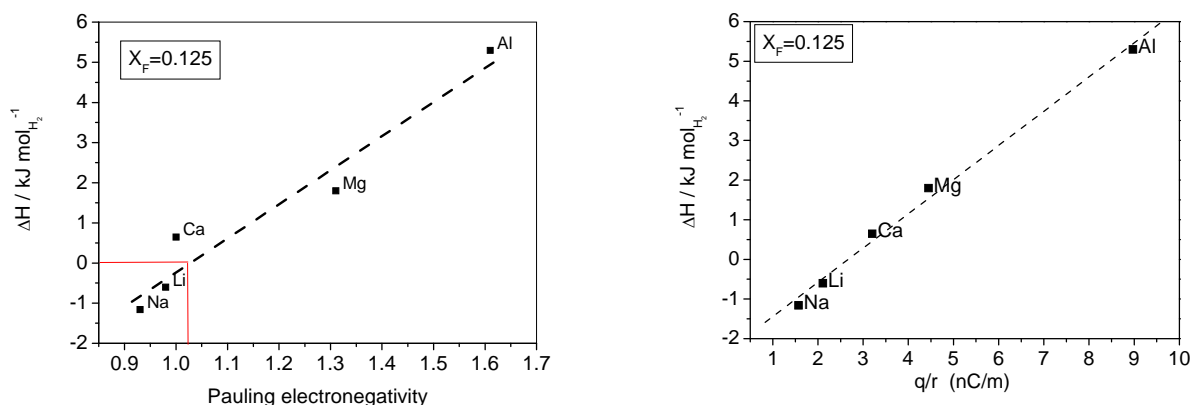


Fig. 22: Enthalpy of mixing for a fixed substitution of 12.5 % of F with H in the hydride as a function of (left) electronegativity and (right) charge density.

### Task 3.3.: Assessment of multicomponent systems

Both stable and unstable borohydrides have been considered:  $\text{LiBH}_4$ ,  $\text{NaBH}_4$ ,  $\text{Ca}(\text{BH}_4)_2$  and  $\text{Mg}(\text{BH}_4)_2$  for the first category and  $\text{Al}(\text{BH}_4)_3$  and  $\text{Zr}(\text{BH}_4)_4$  for the latter.

Concerning stable  $\text{MBH}_4$ , the substitution of fluorine has been modelled for sodium, lithium and calcium. Substitution by chlorine was considered in Li and Ca borohydride, whereas bromine substitution was considered only for  $\text{Ca}(\text{BH}_4)_2$ . For magnesium borohydride, only chlorine substitution has been calculated, due to the parallel work with WP1 and 2.

$\text{LiBH}_4$  has been widely investigated in both orthorhombic (stable at low temperature) and hexagonal (stable at higher temperature) phases. The case of fluorine substitution in orthorhombic  $\text{LiBH}_4$  has been deeply studied and has led to the statement of the locality principle. Indeed, in the unit cell of  $\text{LiBH}_4$  16 hydrogen are present, so generating a very large number of possibilities for the same fluorine substitution. Their classification by symmetry was not enough to significantly reduce the required computational cost. It has been verified that the most stable structures are those where F atoms are all bonded to the same tetrahedron (locality principle, see Fig. 30 for a graphical example).

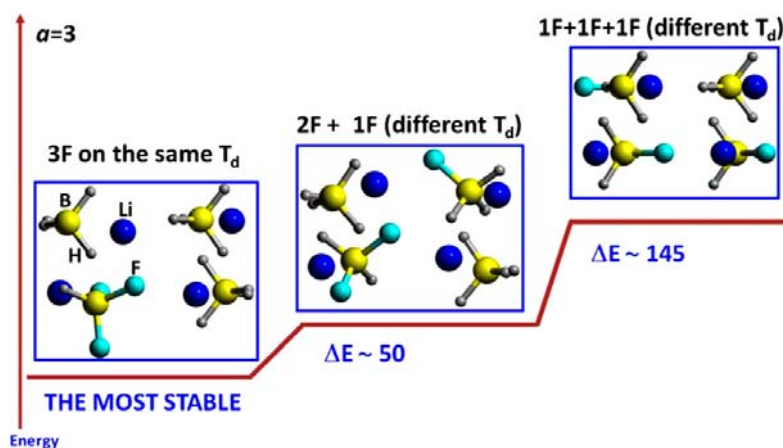


Fig. 23: Graphical example of the locality principle for  $\text{LiBH}_{3.25}\text{F}_{0.75}$ : reported  $\Delta E$  values are based on electronic energy calculations (no ZPE included) and expressed as relative energy with respect to the most stable optimized structure for each composition, normalized to the formula unit. Color coding: Li blue, B yellow, H light grey, F light blue, cell borders in blue.

The presence of fluorine inside orthorhombic  $\text{LiBH}_4$  has a destabilizing effect, with positive values of enthalpy of mixing (with a maximum value of about 17 kJ/mol per formula unit). Considering the hexagonal phase, thermodynamic properties have been computed for F substitution and  $\text{mix}\Delta H$  resulted positive, but lower with respect to the orthorhombic case ( $\text{mix}\Delta H$  lower than 15 kJ/mol per formula unit). For the Cl-substitution in  $\text{LiBH}_4$ , due to the larger steric hindrance of Cl compared to F, it was the entire  $\text{BH}_4$  group which was substituted by Cl. Also in this case, the enthalpy of mixing for both phases was computed. For the orthorhombic phase positive values have been obtained, but much smaller than those computed for the fluorine case (with a maximum of about 1.5 kJ/mol per formula unit); for the hexagonal phase, small negative values of  $\text{mix}\Delta H$  were obtained, less than -1.5 kJ/mol per formula unit.

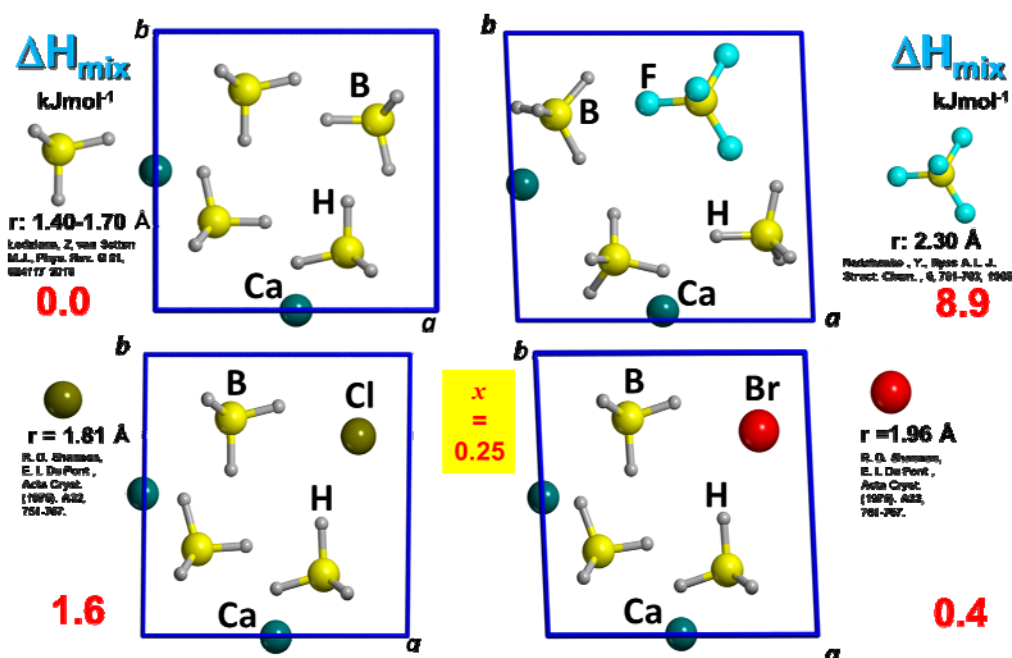


Fig. 24: Schematic representation of the substitution of the  $\text{BH}_4$  unit ( $x=0.25$ ) in  $\text{Ca}(\text{BH}_4)_2$  with fluorine, chlorine and bromine with the respective  $\text{mix}\Delta H$  expressed in  $\text{kJ}\cdot\text{mol}^{-1}$  per formula unit and the ionic radii.

Considering  $\beta\text{-Ca}(\text{BH}_4)_2$ , the effect of the three different halogens substituted, i.e. F, Cl and Br, is summarized in Fig. 24, where  $\text{mix}\Delta H$  are reported for a specific composition ( $x = 0.25$ ), showing that

fluorine has the larger destabilizing effect with respect to chlorine and bromine.

As already mentioned, for the pure  $\alpha$ - $\text{Mg}(\text{BH}_4)_2$  only the substitution of chlorine has been simulated. Due to the large size of the unit cell (330 atoms, see Fig. 25), a different computational approach has been necessary, consisting in the first optimization of only unit cell parameters with the Hartree-Fock (HF) method and the subsequent optimization with the standard DFT PBE functional. To check the results, the hybrid B3LYP functional was also adopted, in single point calculations on the so optimized geometries. No frequency calculations were possible, so the enthalpy of mixing was approximated using electronic energy. Mixing energy values are all negative, so indicating possible miscibility.

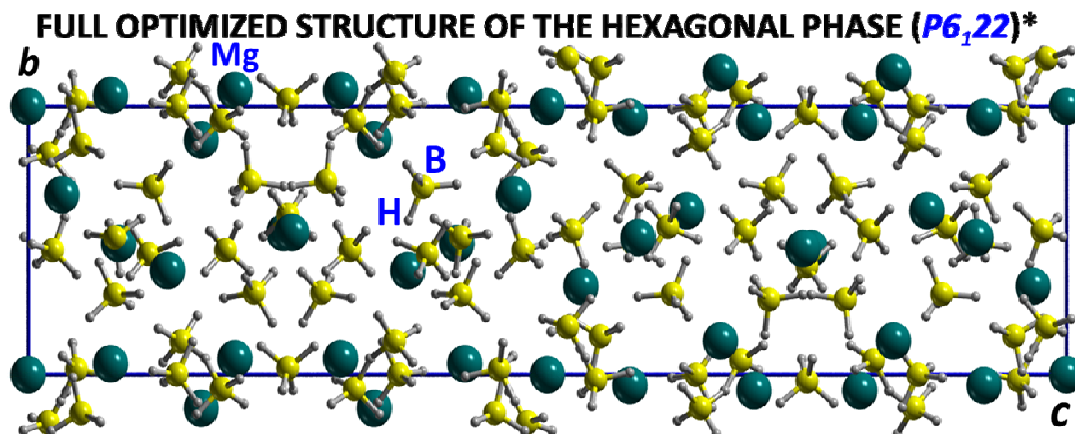


Fig. 25: Optimized unit cell of  $\alpha$ - $\text{Mg}(\text{BH}_4)_2$ , viewed along the  $a$  axis. Mg cyan, B yellow and H grey. Cell borders in blue.

For the unstable borohydrides, only the case of aluminium was examined in terms of fluorine substitution. Indeed, for zirconium borohydride, just the simulation of the structure starting from the resolved atomic coordinates by WP2 has been carried out. The fluorine substitution in  $\text{Al}(\text{BH}_4)_3$  was modelled for a limited number of configurations, chosen by exploiting the locality principle, leading to the conclusion that the fluorine inclusion in the lattice seems to stabilize the compound. On the basis experimental coordinates resolved by WP2 for  $\text{Zr}(\text{BH}_4)_4$  (space group  $P-43m$ ), *ab initio* calculations have revealed a phonon instability, which could be removed by reducing the symmetry to  $P23$ .

### Task 3.4.: Kinetic modelling

Kinetic modelling requires a full description of reaction mechanisms, as well as the determination of activation energies for various reaction steps. The knowledge of thermodynamic quantities can provide useful input for kinetic modelling, e.g. driving force for phase transformations. On the basis of experiments and calculations performed in WPs 1-2 and 3, respectively, it turned out that a full thermodynamic assessment of  $\text{Ca}(\text{BH}_4)_2$  compound was not possible, because of the complicated reaction steps during dehydrogenation. So, the dehydrogenation kinetics of the system selected for the tank production in WP4 was only characterized experimentally in WP2, as described before, but not modelled in WP3.

### Main scientific results

- Calculation of thermodynamics properties for the mixing reaction between pure hydride or borohydride and the corresponding halide, as summarized in Fig. 26 for  $\text{mix}\Delta H$ .

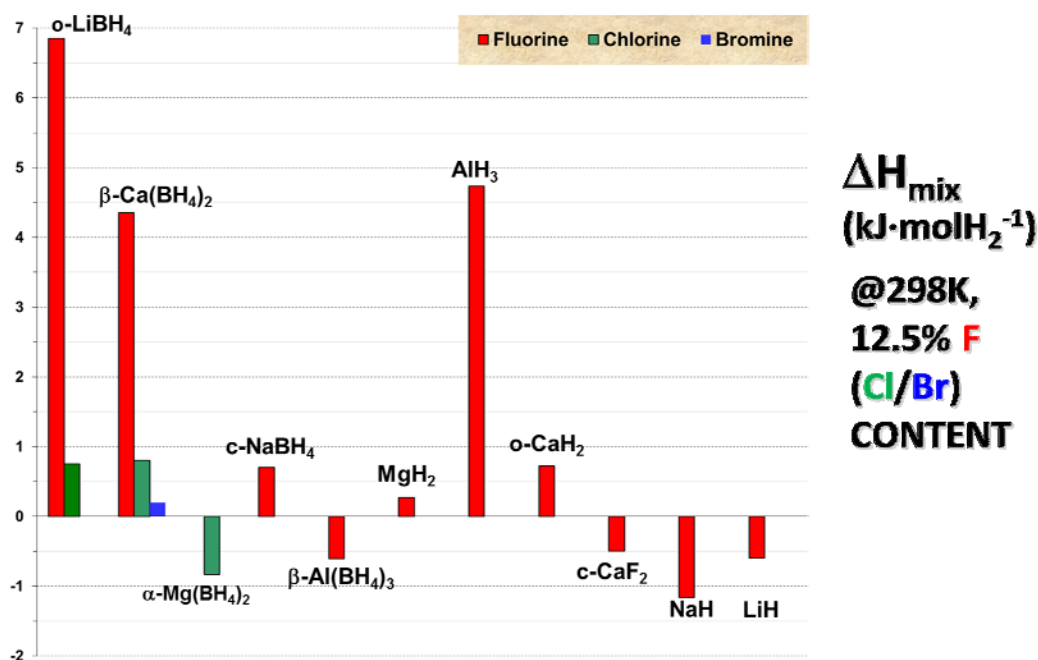


Fig. 26: Conclusive bar chart, summarising the whole situation computed during the FLYHY project, at the 12.5% fluorine content for each case, for the computed variations of enthalpy of mixing, expressed in kJ/molH<sub>2</sub>. In case of CaF<sub>2</sub>, the same content of hydrogen was considered. For comparison, also chlorine and bromine substitutions were reported (green and blue bars, respectively).

- Locality principle statement for the selection of mixed configurations to be computed, tested for LiBH<sub>4</sub>
- Stabilization effect of fluorine in orthorhombic LiBH<sub>4</sub>, Ca(BH<sub>4</sub>)<sub>2</sub>
- The larger the anion the more favourite the substitution, verified in case of Ca(BH<sub>4</sub>)<sub>2</sub>
- Combined quantum-mechanical strategy for the study of larger systems, as Mg(BH<sub>4</sub>)<sub>2</sub>
- Relevance of the dispersion contribution calculation
- Use of the computed IR spectra to assign bands and characterize the measured spectra in WP2, especially for the interpretation of spectra of mixed compounds
- Development of a thermodynamic database by Calphad method, involving pure hydride and fluoride phases, together with some calculated solid solutions
- Calphad calculation of ternary and pseudo-binary phase diagrams.

#### 4.1.6 Work package 4: Techno-Economical Evaluation

##### Objectives of the planned investigations of the work package

The objectives of this work package were

- to find the materials most suitable for applications which have been developed in FLYHY,
- to validate these with respect to storage tank requirements and do a benchmarking with other solid storage materials as well as storage solutions like compressed gas or liquid hydrogen storage;

- to design and construct a prototype hydrogen storage tank, do preliminary test measurements with the optimal material developed in FLYHY on the tank alone, and, if decided upon, test it together with a HT PEM fuel cell,
- evaluate the safety aspects of the materials (e.g. health hazards due to metal powders or formation of halogenic acids or boranes during hydrogen sorption) to draw conclusions for tank construction and give corresponding recommendations for technological implementation;
- To evaluate cost of materials synthesised in FLYHY

#### Task 4.1: Cost, benchmarking of materials

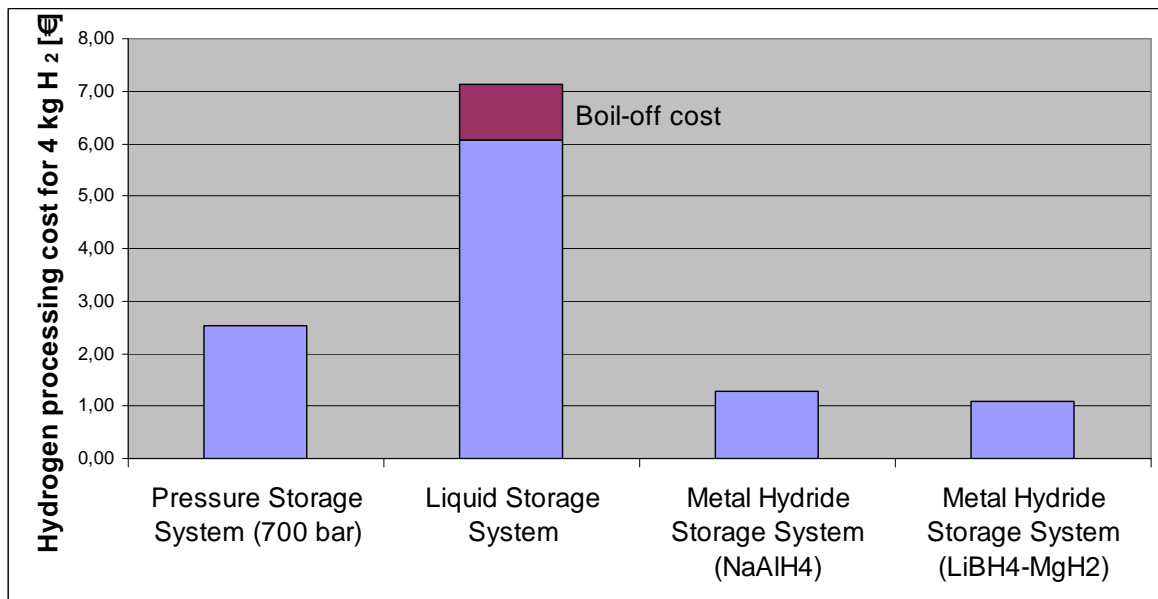


Fig. 27: Hydrogen processing cost per cycle (unique loading and unloading) at a storage capacity of 4 kg H<sub>2</sub> (from <sup>2</sup>)

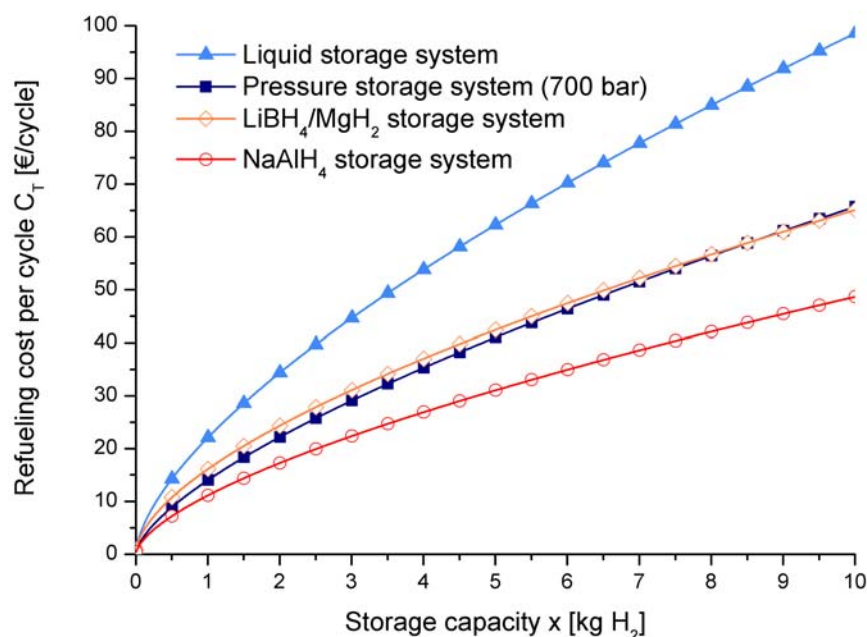


Fig. 28: Cost analysis per loading cycle for different hydrogen storage system solutions. Refuelling cost model includes cost for purchase of hydrogen, processing cost (Fig. 27), tank system and storage material depreciation (from <sup>3</sup>).

Fig. 27 shows the results of calculations of cost for hydrogen processing (pressurising, cooling) per hydrogen loading cycle of different types of hydrogen tanks (from <sup>2</sup>), Fig. 28 results for a complete cost analysis of different storage solutions (from <sup>3</sup>). Over the calculated 1000 loading cycles cost for depreciation of the hydrogen storage material have a lower influence on cost as expenses for hydrogen and its processing.

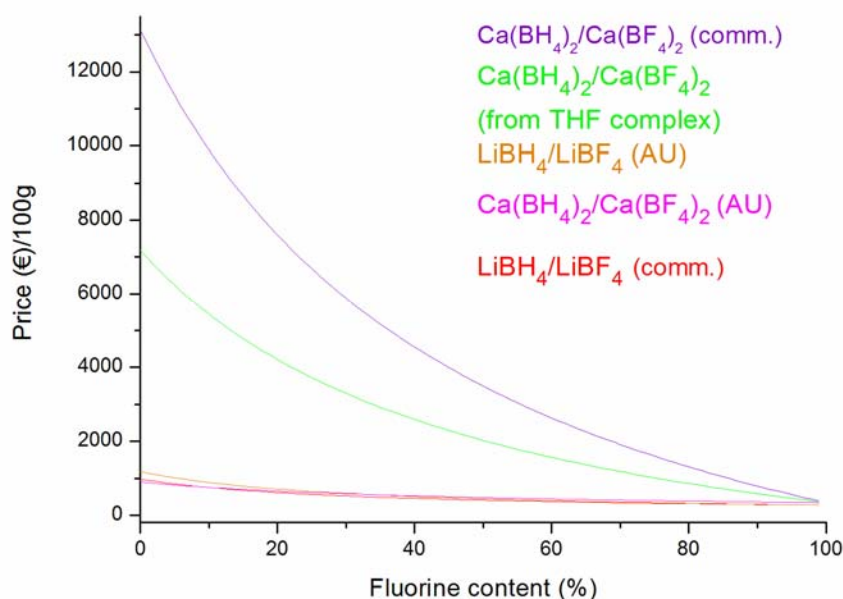


Fig. 29: Comparison of costs for self- synthesis of Li / Caborohydrides and commercially available sources of  $\text{LiBH}_4$  and  $\text{Ca}(\text{BH}_4)_2$ . (comm.) = commercial source. (AU) = synthesized at Aarhus University. The pure commercially available versions of  $\text{Ca}(\text{BH}_4)_2$  (violet/green) are several orders of magnitude too expensive compared to completely self-synthesized materials. Self-synthesized  $\text{LiBH}_4$  however, reaches comparable prices (red vs. orange).

It could be demonstrated by AU that materials synthesising rather than buying the commercially available products is much more advantageous (Fig. 29). The more expensive part of the mixture is the borohydride component, not the borofluoride (all curves converge to approximately the same costs upon larger fluorine content), thus improving borohydride synthesis is highly desirable.

The figure shows, that the pure commercially available versions of  $\text{Ca}(\text{BH}_4)_2$  (violet/green) are several orders of magnitude too expensive compared to completely self-synthesized  $\text{Ca}(\text{BH}_4)_2$  materials. Self-synthesized  $\text{LiBH}_4$  however, reaches comparable prices (red vs. orange).

Cost for FLYHY raw materials, in the range of several 1000 Euros per kg, still today are much higher compared to commercially available room temperature hydrides (in the range of several ten to about 100 – 150 Euro/kg, capacities below 2 wt.%, comparable volumetric capacities up to more than 100 kg  $\text{H}_2/\text{m}^3$ ). The main reasons are the high purity of materials used for synthesis, purchase of only small amounts of high purity materials, and laboratory state of synthesis. (example: pure NaH, lab. quality ca. 300 – 500 € / kg, world market price NaH, 60% suspension in oil ca. 11.000 € / ton, i.e. ca. 18 € / kg of low purity material). In order to become competitive with compressed gas hydrogen storage and to reach the FCH JU target of 500 €/kg of stored  $\text{H}_2$ , e.g. a 10 wt.% material should not cost more than ~40 €/kg to account for the also necessary tank hull (which for solid state hydrogen storage at pressures below 150 bar can be based e.g. on conventional steel tank technology).

<sup>2</sup> J. Jepsen et. al., private communication (GKSS, 2010)

<sup>3</sup> J. Jepsen, J. M. Bellosta von Colbe, T. Klassen, M. Dornheim, "Economic potential of complex hydrides compared to conventional hydrogen storage systems", Int. J. Hydrogen Energy 37 (2012) 4204 - 4214



In future projects, the following potentials for cost reduction for a commercialization of solid state hydrogen storage materials and tanks have to be investigated:

- Systematic investigation and scale-up of the wet chemical synthesis of halogen free boron hydrides with the process, developed at AU (patent application under evaluation).
- Investigation of the influence of impurities on hydrogenation behaviour with the target, to be able to use less pure and thereby cheaper raw materials for synthesis.
- Optimisation of milling times, i.e. using as short as milling time as possible.
- Development of a continuous processing route for materials synthesis instead of batch processing, used today
- Investigation of mills with low energy consumption, i.e. e.g. vibration mills, which could be much more energy efficient than planetary ball mills, as results from HZG already have demononstrated in another project (e.g. 4)

Further trivial options to reduce investment cost for solid state storage are:

1. cost reduction by purchasing larger amounts of raw materials (kg or tonnage quantities instead of 100 g);
2. cost reduction by cheaper suppliers then fine chemical companies (e.g. from China);

#### Task 4.2: Determination of tank relevant properties

In order for a first evaluation of cyclability, the RHC system  $3\text{CaH}_2 + 4\text{MgB}_2 + \text{CaF}_2$  (material from the batch, that was filled in the prototype tank) was investigated by a volumetric technique (Sievert's type measurements). The material was subjected to five absorption and 4 desorption cycles. The applied temperature and hydrogen pressure conditions were 400 °C and 130 bar during absorption and 400°C and 5 bar during desorption. Fig. 30 reports the normalized hydrogen absorption curves. The curves

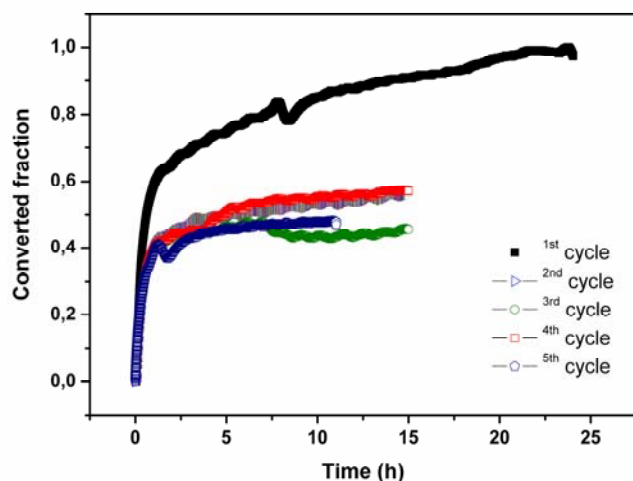


Fig. 30: Absorption kinetic of the  $3\text{CaH}_2 + 4\text{MgB}_2 + \text{CaF}_2$  system. The measurement was performed at 400 °C under 130 bar of hydrogen.

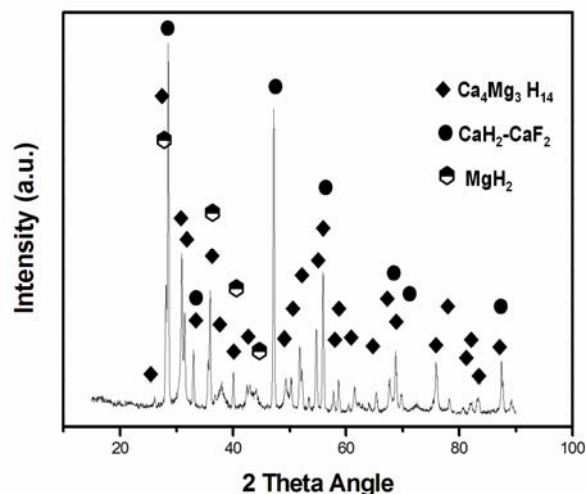


Fig. 31: XRD analysis of the material after the 5<sup>th</sup> absorption cycle.

<sup>4</sup>) N. Eigen, C. Keller, M. Dornheim, T. Klassen and R. Bormann, "Industrial production of light metal hydrides for hydrogen storage", Viewpoint paper in Scripta Materialia, 56 (10) (2007) 847-851; DOI: <http://dx.doi.org/10.1016/j.scriptamat.2007.01.024>; <http://dvsun3.HZG.de/journals/2007/Eigen-scriptmat.pdf>

are normalized to the absorption capacity measured during the first absorption cycle (7 wt.%). The theoretical hydrogen gravimetric capacity of the system is 7.7 wt.%. The reason of the not completely achieved capacity during the first absorption cycle resides in the resistance of the  $\text{CaF}_2$  to react with the  $\text{MgB}_2$ . After the first absorption a marked decrement of the hydrogen capacity is visible in the second cycle. This is due to the formation of unreactive amorphous boron and  $\text{CaB}_{12}\text{H}_{12}$  during desorption. Anyway, it must be noticed that after the first absorption cycle the system hydrogen capacity remains almost constant. Fig. 31 shows the XRD analysis of the hydrogenated material after the 5<sup>th</sup> cycle.

The crystalline phases present in the absorbed material are  $\text{Ca}_4\text{Mg}_3\text{H}_{14}$ ,  $\text{MgH}_2$  and the solid solution  $\text{CaH}_2\text{-CaF}_2$ . From this analysis appears clear that the phases responsible for the hydrogen storage capacity observed after the first cycle are  $\text{Ca}_4\text{Mg}_3\text{H}_{14}$  and  $\text{MgH}_2$ . Further details on the reaction pathway in this material are given in the section on “Halogen substituted hydrides based on Reactive Hydride Composites (RHC)”, page - 11 -.

Compacted pellets of the system  $3\text{CaH}_2 + \text{CaF}_2 + 4\text{MgB}_2$  were prepared in order to study the influence of compaction on hydrogenation properties and thermal conductivity. The theoretical bulk density of this fluorine doped Ca-based RHC is  $2.27 \text{ g/cm}^3$ . While loose powder has a density of around  $1.03 \text{ g/cm}^3$ , by compaction the material density increases to about  $1.55 \text{ g/cm}^3$ . Therefore, the volume of the pores of the material can be estimated as equal to 32 % and 55 % of the total volume occupied by the material respectively for the compacted powder and for the loose powder.

In sight of a future employment of the system  $3\text{CaH}_2 + \text{CaF}_2 + 4\text{MgB}_2$  as a hydrogen storage material for onboard application, the study of its thermal conductivity is of crucial importance. In fact, as for all the other metal hydrides or mixtures of metal hydrides, the temperature has a profound impact on reaction kinetics, therefore heat production and transfer within the tank must be investigated. For these reasons, the thermal conductivity of the system  $3\text{CaH}_2 + \text{CaF}_2 + 4\text{MgB}_2$  was measured both for the loose powder and for the compacted one. The thermal conductivity analysis was performed using a Hot Disk TPS 1500 from Thermal Constants Analyser. The thermal conductivity of the system  $3\text{CaH}_2 + \text{CaF}_2 + 4\text{MgB}_2$  as loose powder was determined as ca  $0.125 \text{ W/(m}\cdot\text{K)}$ , whereas that of the compacted material was ca.  $0.5 \text{ W/(m}\cdot\text{K)}$  was recorded. As expected, the compaction of the material sensibly enhances the thermal conductivity of the system. These data represent an important base for the modeling of the heat transfer during the hydrogen absorption and desorption processes in the mixed system  $3\text{CaH}_2 + \text{CaF}_2 + 4\text{MgB}_2$ .

#### Task 4.3. Safety

Conclusions and safety actions to be taken in comparison with room temperature hydrides ( $\text{TiCrMn}$ ,  $\text{FeTi}$ ,  $\text{LaNi}_5$  alloys etc.) were drawn from the analysis of the handling procedures at the different partners preparing materials. The handling of the metal powders has to be performed under inert gas atmosphere always (e.g. Ar), to account for flammability as well as oxygen and moisture sensibility of the materials. In the wet chemistry processing routes, also the introduction of solvents increases the risk of larger fires or an explosion, due to the nature of most solvents (volatility and flammability of e.g. diethyl ether, hydrocarbons, amines etc.). Spills in working areas are potentially more complicated due to evaporation, in turn leading to a spread of e.g. toxic substances, lachrymators or extremely bad odour ( $\text{Me}_2\text{S}$  for an example). Cleaning after spillage must be performed fast and efficiently and can incur negative complications for special apparatus if not taken care of immediately and correctly (e.g. glovebox solvent spills are difficult to handle due to limited tools for cleaning and can be harmful if left untreated). The use of HF and/or HF-related agents should never be left to untrained personnel due to the severe harmful effects of HF-burns and the potential introduction of F ions into human tissue which ultimately can be fatal or have grave consequences. It should be stressed however, that many related chemicals (e.g.  $\text{Et}_3\text{N}\cdot 3\text{HF}$ ) are considered safe to use for regular personnel. The use of anhydrous HF or HF (aq) is considered to be very dangerous and should never be done without the proper training and safety, e.g. HF dissolves glass equipment and therefore all handling must be done

in teflon equipment or stainless steel. Here we have not been employing HF in other forms than  $\text{Et}_3\text{N} \cdot 3\text{HF}$ .

For production units, the following gas sensors have to be foreseen:

- Hydrogen in all rooms / facilities where powders are handled and experiments to be performed
- Oxygen and water to control purity of inert gas.
- Boranes
- Halogenic acids
- Washing of exhaust gases of test facilities and production units / neutralization of acids is necessary. All metal powders have to be neutralized/oxidized in a controlled manner before giving them to the chemistry waste, e.g. by slow oxidation in a safe container.

The storage tanks and the test facility were designed to withstand internal pressures of up to 200 bars, and internal temperatures up to 400°C of the storage tank (c.f. Task 4.4): This implicates that:

- temperatures of heat exchange media up can be up to 400°C, so specialized oils have to be used. Safety measures for handling oils at these temperatures to be obeyed.
- as materials: common heat resistant stainless steel could be used ( $\Rightarrow$  cost! workability by SME!), as used for chemical processing under elevated temperatures.
- the tank body has to be designed for operation of up to 200 bar and the high temperatures mentioned before

#### Task 4.4. Tests in laboratory prototype tank

##### Materials for prototype tank tests

The FLYHY consortium decided to choose a Ca-based F modified RHC with input composition of  $\text{CaF}_2 + 3\text{CaH}_2 + 4\text{MgB}_2$ , which was prepared by reactive ball milling comparably to the description in section on “Halogen substituted hydrides based on Reactive Hydride Composites (RHC)”, page - 11 - . Further properties can be found in Task 4.2: Determination of tank relevant properties.

##### Prototype solid state hydrogen storage tank

A simple prototype tank, consisting of the interior hull, a cylinder with a diameter of 64 mm, 52 mm internal diameter and a length of 117 mm included in an outer hull for submerging the tank in heating oil, a temperature sensor, withstanding 500°C, and a hydrogen inlet, submerged directly into the hydrogen storage material, was constructed (**Fehler! Verweisquelle konnte nicht gefunden werden.**). The storage material was filled in as a loose powder.

Due to late delivery of the test tank and problems with mounting it to the tank test facility at HZG, no results on performance of the tank could be achieved during the runtime of the project. Test are planned, as soon as these problems have been resolved.

##### Test bench & fuel cell

Due the necessity for testing of the prototype tank first at HZG, it was not possible during the runtime of the project, to attach the prototype tank to the FC test bench (Fig. 32). Therefore no results on the integrated system were obtained during the runtime of the project.

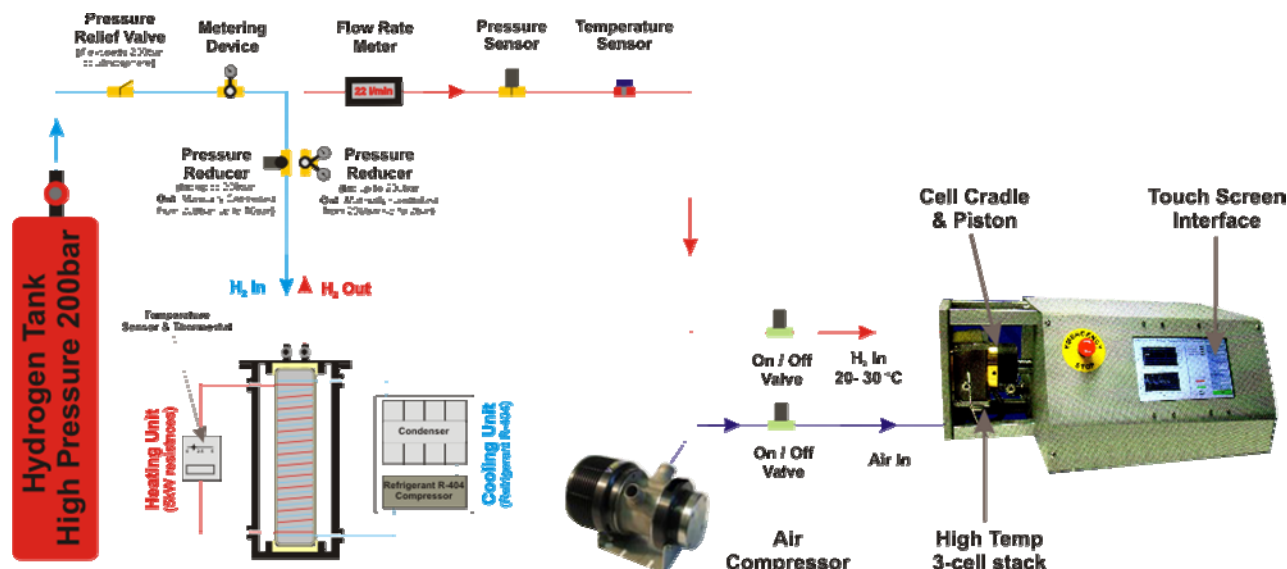


Fig. 32: Sketch of solid state hydrogen storage and fuel cell test bench.

#### 4.1.7 Main scientific results

##### Cost of materials

- The new synthesis routes for halogen substituted borohydrides, developed in FLYHY, show a significant potential for reducing cost compared to commercially available raw materials.
- Cost estimates show, that, compared to high pressure or liquid hydrogen storage, even today solid state storage is competitive, due to lower cost for hydrogen processing (i.e. low pressure hydrogen supply instead of 700 bar or liquid hydrogen) over the targeted lifetime of a tank of at least 1000 cycles. Furthermore, due to much simpler tank design, solid state storage offers especially European SME's new market chances.
- Currently, the potential for cost reductions of FLYHY raw materials is unclear, as up to now there exists no large scale commercial market for e.g. borohydrides. Significant cost reductions are anticipated by using materials with less purity and being available in larger quantities on the world market, as well as e.g. from optimised routes for materials synthesis. Investigations of effects of these impurities on materials properties have to be performed in future projects.

##### Materials for prototype test tank

- The Ca-based RHC chosen for tank testing ( $\text{CaF}_2 + 3\text{CaH}_2 + 4\text{MgB}_2$ ) showed a 50% in hydrogen storing capacity upon the first hydrogen loading / unloading cycle, then remaining constant over the next 4 cycles tested. The reaction pathway responsible for this decrease in capacity could be clarified and is described in WP2, Halogen substituted hydrides based on Reactive Hydride Composites (RHC), page - 11 -.
- Density of the loose powder is around  $1 \text{ g/cm}^3$ , after compaction about  $1,5 \text{ g/cm}^3$ . By compaction the porosity is reduced from ca. 55% down to 32%, increasing thermal conductivity from ca.  $0,125 \text{ W/(m}^{\circ}\text{K)}$  up to ca.  $0,5 \text{ W/(m}^{\circ}\text{K)}$ . These results are important for future simulation and design of tanks based on this type of material.

##### Prototype test tank

- Due to late delivery of the prototype tank and problems with attaching the tank to the test facility at HZG, no data on tank and materials performance could be obtained during the runtime of the project. These tests are planned for spring 2012.

## **4.1.8 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**

### **4.1.8.1 Potential impact and exploitation of results**

The investigations made in FLYHY point towards that fluorine incorporation is affecting the stability of the materials significantly, i.e. the decomposition temperatures have been decreased drastically, e.g. by mixing metal tetrafluoroborates with metal borohydrides, or by adding simple fluorides in the synthesis of Reactive Hydride Composites. The larger halides (Cl, Br, I) appear to mainly affect the hydrogenation properties to the extent that some improvements in reversibility have been observed. Overall, this could be interpreted as a result of two types of substitution: large halides (Cl, Br, I) substituting for  $\text{BH}_4^-$  units, and fluorine substituting for individual hydrogen atoms.

A mixture such as  $\text{NaBH}_4\text{-NaBF}_4$  exhibits the best of both worlds; strongly destabilised borohydride material, improved rehydrogenation properties and release of large amounts of hydrogen. In accordance with the different types of metal borohydrides and tetrafluoroborates available, the potential of combining different metals in these mixtures should be tested, e.g. mixing  $\text{LiBF}_4$  with any other available metal borohydride, in order to screen optimal mixture compositions.

Also the findings in Reactive Hydride Composites implicate, that F not only strongly influences reaction kinetics and thermodynamics, but also can change completely the reaction pathway. Therefore more detailed investigations of the dependence of the reaction pathways on hydrogenation temperature and pressure are necessary, to fully exploit the positive effects of fluorine addition.

The experience gathered and the synthetic method development (AU-patent) allows for easier and cheaper access to stable borohydride materials in the future. The prospect of applying the method for larger scale production is attractive and is kept in mind for the patent. The vapour deposition technique employed for the synthesis of  $\text{Zr}(\text{BH}_4)_4$  could also be exploited for attempting to synthesize related unstable (less stable) metal borohydrides in the future.

In summary, FLYHY lead to a significant increase in fundamental knowledge on the positive effects of halogen substitution in high capacity storage materials, and opened up routes to follow in future optimisation of the materials in follow-up research projects like the recently approved FCH JU project BOR4STORE (like FLYHY coordinated by HZG, grant negotiations in final phase).

Whereas the developed routes for materials synthesis now can be optimised, and – provided interest from industry – scaled-up and transferred to industrial production, there is still need for more fundamental investigations on the materials themselves, finding proper additives and producing the materials from cheaper raw materials, to in the end deliver a competitive hydrogen storage technology based on the materials investigated in FLYHY. The developed mechano-chemical routes for materials synthesis are very appropriate for industrial use by SME's.

The simple storage tank technology, employed in FLYHY, is also very suitable for manufacturing by SME's like partner TROPICAL, which is in strong contrast to the complicated manufacturing technology of composite high pressure storage tanks. Especially in stationary applications where weight is only relevant in the second line, this opens up a new market for companies being experienced in construction of e.g. pressurised steel containers and heat exchangers.

### **4.1.8.2 Main Dissemination Activities**

The main dissemination activities of FLYHY 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.



## Publications

### Peer reviewed papers

1. L. Mosegaard, D. Ravnsbæk, Y. Filinchuk, R. T. Vang, Y. Cerenius, F. Besenbacher, H. J. Jacobsen, J.-E. Jørgensen, T. R. Jensen, "Structure and Dynamics in the Solid Solution  $\text{LiBH}_4 - \text{LiCl}$ ", *Chem. Mater.*, 21 (24) (2009) pp 5772 – 5782, DOI: [10.1021/cm902013k](https://doi.org/10.1021/cm902013k)
2. R. Gosalawit, J. M. Bellosta von Colbe, M. Dornheim, T.R. Jensen, Y. Cerenius, K. Suarez, C.M. Bonatto Minella, M. Peschke, R. Bormann, "LiF-MgB<sub>2</sub> system for Reversible Hydrogen Storage", *Journal of Physical Chemistry C* 114 (2010) 10291-10296. DOI: [10.1021/jp910266m](https://doi.org/10.1021/jp910266m).
3. Marcello Baricco, Mauro Palumbo, Eugenio Pinatel, Marta Corno, Piero Ugliengo, "Thermodynamic Database for Hydrogen Storage Materials", *Advances in Science and Technology*, 72 (2010, Trans Tech Publications Inc., Stafa-Zurich) p.213-218, doi:[10.4028/www.scientific.net/AST.72.213](https://doi.org/10.4028/www.scientific.net/AST.72.213),
4. Fønne, J.E.; Corno, M.; Grove, G.; Pinatel, E.; Sørby, M.H.; Ugliengo, P.; Baricco, M.; Hauback, B.C., "Experimental and computational investigations on the  $\text{AlH}_3/\text{AlF}_3$  system", *Journal of Alloys and Compounds*, 509, 1 (Elsevier, Amsterdam, 5 January 2011) 10 – 14 (DOI: [10.1016/j.jallcom.2010.08.147](https://doi.org/10.1016/j.jallcom.2010.08.147)).
5. Line H. Rude, Y. Filinchuk, M. Sørby, B. Hauback, F. Besenbacher, and T.R. Jensen, "The Effect of Anion Substitution in Metal Borohydrides", *Proceedings: Am. Chem. Soc., Div Fuel Chem.* 2010, 55 (2), p.96 - 97
6. Gosalawit-Utke, R.; Suarez, K.; Bellosta von Colbe, J.M.; Boesenberg, U.; Jensen, T.R.; Cerenius, Y.; Bonatto Minella, C.; Pistidda, C.; Barkhordarian, G.; Schulze, M.; Klassen, T.; Bormann, R.; Dornheim, M.: " $\text{Ca}(\text{BH}_4)_2\text{-MgF}_2$  Reversible Hydrogen Storage: Reaction Mechanisms and Kinetic Properties". *Journal of Physical Chemistry C*, 115 (9), (ACS Publications, Washington DC, 2011) 9, 3762 - 3768. (DOI: [10.1021/jp108236e](https://doi.org/10.1021/jp108236e))
7. Rude, L.H.; Nielsen, T.K.; Ravnsbæk, D.B.; Bösenberg, U.; Ley, M.B.; Richter, B.; Arnbjerg, L.M.; Dornheim, M.; Filinchuk, Y.; Besenbacher, F.; Jensen T.R., "Tailoring properties of borohydrides for hydrogen storage: A review", *Phys. Status Solidi A*, 208, (8), (Wiley Blackwell, Hoboken, NJ, USA, 11 July 2011) 1754 - 1773 (DOI: [10.1002/pssa.201001214](https://doi.org/10.1002/pssa.201001214))
8. Rude, L.H.; Filinchuk, Y.; Sørby, M.H.; Hauback, B.C.; Besenbacher, F.; Jensen, T.R., "Anion substitution in  $\text{Ca}(\text{BH}_4)_2\text{-CaI}_2$ : Synthesis, structure and stability of three new compounds", *Journal of Physical Chemistry C*, 115 (15), (ACS Publications, Washington DC, March 29, 2011) 7768-7777, (DOI: [10.1021/jp111473d](https://doi.org/10.1021/jp111473d))
9. Ravnsbæk, D.B.; Rude, L.H.; Jensen, T.R.; "Chloride substitution in sodium borohydride", *J. Solid State Chem.*, 184, 7 (Elsevier, Amsterdam, 30 May 2011) 1858-1866, (DOI: [10.1016/j.jssc.2011.05.030](https://doi.org/10.1016/j.jssc.2011.05.030))
10. Rude, L.H.; Groppo, E.; Arnbjerg, L.M.; Ravnsbæk, D.B.; Malmkjær, R.A.; Filinchuk, Y.; Baricco, M.; Besenbacher, F.; Jensen, T.R., "Iodide substitution in lithium borohydride", *Journal of Alloys and Compounds*, 509, 33, (Elsevier, Amsterdam, 1 June 2011) 8299-8305 (DOI: [10.1016/j.jallcom.2011.05.031](https://doi.org/10.1016/j.jallcom.2011.05.031))
11. M. Corno, E. Pinatel, P. Ugliengo, M. Baricco, "A computational study on the effect of fluorine substitution in  $\text{LiBH}_4$ ", *Journal of Alloys and Compounds*, 509, Supplement 2, (Elsevier, Amsterdam, September 2011), S679–S683, (DOI: [10.1016/j.jallcom.2010.10.005](https://doi.org/10.1016/j.jallcom.2010.10.005))
12. Olena Zavorotynska, Marta Corno, Alessandro Damin, Giuseppe Spoto, Piero Ugliengo, Marcello Baricco. "Vibrational properties of  $\text{MBH}_4$  and  $\text{MBF}_4$  crystals (M=Li, Na, K): a combined DFT, infrared and Raman study", *Journal of Physical Chemistry C*, (ACS Publications, Washington DC, 2011), 115 (2011) 18890–18900, (DOI: [10.1021/jp2058244](https://doi.org/10.1021/jp2058244))



13. Rude, L.H.; Zavorotynska, O.; Arnbjerg, L.M.; Ravnsbæk, D.B.; Malmkjær, R.A.; Grove, H.; Hauback, B.C.; Baricco, M.; Filinchuk, Y.; Besenbacher, F.; Jensen, T.R., "Bromide substitution in lithium borohydride,  $\text{LiBH}_4\text{-LiBr}$ ", Int. J. Hydrogen Energy ((Elsevier, Amsterdam, 2011), 36 (24), (2011) 15664-15672, DOI: [10.1016/j.ijhydene.2011.08.087](https://doi.org/10.1016/j.ijhydene.2011.08.087)
14. K. Suarez Alcantara, U.Boesenberg, O.Zavorotynska, J. Bellosta von Colbe, K.Taube, M.Baricco, T. Klassen, M. Dornheim: "Sorption and desorption properties of a  $\text{CaH}_2/\text{MgB}_2/\text{CaF}_2$  Reactive Hydride Composite as potential hydrogen storage material", Journal of Solid State Chemistry, 184 (11), (2011) 3104-3109 . (DOI: [10.1016/j.jssc.2011.09.019](https://doi.org/10.1016/j.jssc.2011.09.019) )
15. Ivan Saldan, Renato Campesi, Olena Zavorotynska, Giuseppe Spoto, Marcello Baricco, Anna Arendarska, Klaus Taube, Martin Dornheim, "Enhanced hydrogen uptake/release in  $2\text{LiH-MgB}_2$  composite with titanium additives", Int J of Hydrogen Energy (2012) 37 (2012) 1604-1612, [doi:10.1016/j.ijhydene.2011.10.047](https://doi.org/10.1016/j.ijhydene.2011.10.047)
16. Ivan Saldan, "A prospect for  $\text{LiBH}_4$  as on-board hydrogen storage", Cent. Eur. J. Chem., 9(5) (2011) 761-775, DOI: [10.2478/s11532-011-0068-9](https://doi.org/10.2478/s11532-011-0068-9)

### Publications (submitted/accepted)

- Suarez Alcantara, Karina; Ramallo Lopez, Jose; Bösenberg, Ulrike; Saldan, Ivan; Pistidda, Claudio; Jensen, Torben; Cerenius, Yngve; Sørby, Magnus; Bellosta von Colbe, José; Taube, Klaus; Klassen, Thomas; Dornheim, Martin, " $3\text{CaH}_2+4\text{MgB}_2+\text{CaF}_2$  Reactive Hydride Composite as a Potential Hydrogen Storage Material: Hydrogenation and Dehydrogenation Pathway", accepted for publication in The Journal of Physical Chemistry
- Saldan, Ivan; Gosalawit-Utke, Rapee; Pistidda, Claudio; Bösenberg, Ulrike; Ramallo Lopez, Jose; Requejo, Felix; Schulze, Matthias; Avila, José; Jensen, Torben; Suarez, Karina; Bellosta von Colbe, José; Taube, Klaus; Dornheim, Martin; Klassen, Thomas, "Influence of Stoichiometry on the Hydrogen Sorption Behavior in the  $\text{LiF-MgB}_2$  System", Submitted to The Journal of Physical Chemistry
- I. Saldan, O. Zavorotynska, G. Spoto, M. Baricco, K. Taube, T. Klassen, M. Dornheim, "Hydrogen sorption in  $\text{LiF-LiH-MgB}_2$  and  $\text{LiF-MgB}_2-0.1\text{X}$  ( $\text{X} = \text{TiF}_4; \text{TiO}_2; \text{TiN}; \text{TiC}; \text{TiB}_2$ ) composites", submitted to The Journal of Physical Chemistry

### Talks:

1. Invited lecture:  
Torben Jensen, "New Materials for Hydrogen Storage - Novel materials, Nanoconfinement, Anion substitution explored with powder X-ray diffraction", 6th Empa Symposium Hydrogen & Energy, Stoos, Switzerland, 2012, 22-27. Januar 2012
2. Invited lecture:  
C. Frommen, M.H. Sørby, B.C. Hauback, "Structural and decomposition studies of novel borohydrides", SCTE 2010, Annecy, France, September 2010
3. Invited lecture:  
M.H. Sørby, N. Aliouane, C. Frommen, S. Deledda, J.E. Fonnelløp, H. Grove, I. Llamas-Jansa, K. Lieutenant, S. Sartori, H. Østby, B.C. Hauback, "Synthesis and characterization of novel borohydrides", E-MRS, Warsaw, Poland, September 2010
4. Invited lecture  
Torben Jensen, "A renewable energy-system based on hydrogen as an energy carrier", Third International Nanoscience Conference (INASCON). Sursee, Lucerne, Switzerland, 20 - 23 August 2009.

5. Invited lecture:  
Martin Dornheim, "Reaction mechanism and kinetics of  $\text{MgH}_2 + (\text{Ca}, \text{Na}, \text{Li})$  borohydride RHCs", Gordon Research Conference on Hydrogen-Metal Systems, Lucca, Italy 2009
6. Keynote lecture  
Martin Dornheim, "Reaction mechanism and kinetics of  $\text{MgH}_2$ /borohydrides based Reactive Hydride Composites", MH2010, 12<sup>th</sup> International Symposium "Metal-Hydrogen Systems - Fundamentals and Applications", Moscow, July, 19-23 2010
7. Invited lecture  
Torben R. Jensen, „Mixed-metal boron-based hydrides as potential future hydrogen storage materials“, SMEC2009 study of matter at extreme conditions, Miami - Western Caribbean. March 28 - April 2, 2009.
8. Invited lecture:  
K. Taube: Nanostructured Materials for Solid State Hydrogen Storage. In: EuroNanoForum 2009, Nanotechnology for Sustainable Economy. Prag (CZ), 02.-05.06.2009, 2009.
9. K. Taube; M. Dornheim: "Reaction mechanism and kinetics of  $\text{MgH}_2$ /borohydride based reactive hydride composites", 1st International Conference on Materials for Energy, ENMAT 2010. Karlsruhe (D), 04.-08.07.2010, 2010.
10. K. Lieutenant, S. Deledda, C. Frommen, H. Grove, I. Llamas-Jansa, S. Sartori, M.H. Sørby, B.C. Hauback, "Structural studies of hydrogen storage materials using neutron scattering", Neutrons for Global Energy Solutions, NGES, Bonn, Germany, September 2010
11. S. Hino, J.E. Fonnelløp, B. Richer, T.R. Jensen, M.H. Sørby, B.C. Hauback, "Halide substitution in  $\text{Mg}(\text{BH}_4)_2$ ", 8<sup>th</sup> Nordic Center of Excellence on Hydrogen Storage Materials meeting, Uppsala, Sweden, October 2010
12. Line H. Rude, Yaroslav Filinchuk, Torben R. Jensen, "Anion substitution - a new tool to tailor the properties of hydrogen storage materials", iNANO Autumn school, 8/10-11/10-2010
13. Martin Dornheim, "Kinetic optimization of  $\text{LiBH}_4/\text{MgH}_2$  and  $\text{Ca}(\text{BH}_4)_2/\text{MgH}_2$  Reactive Hydride Composites", Task 22 IEA HIA EXPERT MEETING, Fremantle, WA, Australia, 16-20 January 2011
14. José Bellosta von Colbe, "Materials aspects in complex hydride based hydrogen storage tanks", Task 22 IEA HIA EXPERT MEETING, Fremantle, WA, Australia, 16-20 January 2011
15. Dornheim, M.; Boesenberg, U.; Goslawit, R.; Suarez, K.; Pistidda, C.; Bonatto Minella, C.; Karimi, F.; Pranzas, K.; Barkhordarian, G.; Saldan, I.; Arendarska, A.; Puzkiel, J.; Bellosta von Colbe, J.; Lozano, G.; Jepsen, J.; Metz, O.; Walcker-Mayer, S.; Taube, K.; Klassen, T.: "Development and Characterization of Novel Hydrogen Storage Materials and Systems". In: 2011 MRS Spring Meeting. San Francisco, CA (USA), 25.-29.04.2011, 2011.
16. Marta Corno, "First principles prediction of structural, vibrational and thermodynamic properties of mixed metal hydrides and fluorides", 5th Symposium Hydrogen & Energy, Stoos (CH), January 23-28, 2011
17. Marcello Baricco, "Experimental and theoretical studies on hydrogen storage materials.", Task 22 IEA HIA EXPERT MEETING, Fremantle, WA, Australia, 16-20 January 2011
18. T. R. Jensen, *Novel series of bi-metal borohydrides and nanoconfinement*, International Energy Agency HIA Expert Meeting, Task 22, Fremantle, Australia, 16 – 20/1 2011
19. T. R. Jensen, *Nanoconfinement and novel series of bi-metal borohydrides*, The International Chemical Congress of Pacific Basin Societies, Alternate Energy Technology symposium, Advances in Chemistry and Materials for Hydrogen Storage, Honolulu, Hawaii, USA , 16 – 20/1 2011

20. Rude, L.H.; Groppo, E.; Arnbjerg, L.M.; Filinchuk, Y.; Baricco, M.; Jensen, T.R. *Tailoring hydrogen storage properties by anion substitution of the heavier halides*, 8th meeting of 'Nordic Center of Excellence on Hydrogen Storage Materials', Uppsala, Sweden., 16 – 20/1 2011
21. T. R. Jensen, *Fossil fuels - renewable energy – Hydrogen*, The 3rd Chalmers-ISIS Workshop: Neutron Scattering and Materials for Energy Applications, Göteborg, Sweden , 22-24/9 2010
22. T. R. Jensen, *Hydrogen – a possible future energy carrier*, The Annual Meeting of the Swiss Society For Crystallography, 'New Materials for Clean Future', Geneva, Switzerland, 17/9 2010
23. T. R. Jensen, *Novel materials - The only hope for a clean and sustainable future*, 2010 EMRS Fall Meeting - Symposium H: Novel Materials for Alternative Energy, Warsaw, Poland, 13-17/9 2010
24. T. R. Jensen, *Metal hydrides and complex hydrides for hydrogen storage*, Department of Advanced Materials and Technologies, Military University of Technology (MUT), Warsaw, Poland, 14/9 2010
25. T. R. Jensen, *Hydrogen storage updates*, Meeting in the Centre for Energy Materials, Århus, Denmark, 3/9 2010
26. T. R. Jensen, *Hydrogen storage materials*, 12<sup>th</sup> European Powder Diffraction Conference, Darmstadt, Germany , 27-30/8 2010
27. Rude, L.H.; Filinchuk, Y.; Sørby, M; Hauback, B.C.; Besenbacher, F.; Jensen, T. R. *Effect of anion substitution in metal borohydrides*, ACS Fall 2010 National Meeting and Exposition, Boston, USA, 22-26/8 2010
28. Rude, L.H.; Filinchuk, Y.; Sørby, M; Hauback, B.C.; Jensen, T. R. *The effect of anion substitution in metal borohydrides*, MH2010 International symposium on metal-hydrogen systems, Moscow, Russia, 19-23/7 2010
29. T. R. Jensen, “Hydrogen opbevaring Med fokus på mobile anvendelser, Energi Horsens Fonden, Vitus Bering Innovation Park, Chr. M. Østergaardsvej, 4A, 8700 Horsens, Danmark, 6/2-2012.
30. T. R. Jensen, “Hydrogen storage New approaches for mobile applications, 9th Hydrogen Link workshop: Hydrogen for Transportation status, potential and research opportunities, 1. december 2011, Risø-DTU, Roskilde, Denmark.
31. T. R. Jensen, “Hydrogen-samfundet - et nyt energisystem, Nanorama Fredagsforedrag, iNANO, Aarhus University, 26. August 2011.
32. T. R. Jensen, “Hydrogen in Denmark and Scandinavia”, International Energy Agency HIA Expert Meeting, Task 22, The Royal Danish Academy for Science and Letters, Copenhagen, Denmark, 4-8 September 2011
33. Klaus Taube, GKSS, “Nanostructured Materials for Solid State Hydrogen Storage“, EuroNanoForum 2009, Session “A3 2.2 Nanotechnology for Energy - Nanotechnology for H2 Production & Storage; Fuel cells“, Prague, June, 2 – 5, 2009
34. J. E. Fonnelløp, S. Sartori, M. H. Sørby, B. C. Hauback, “Effect of fluorine additives on the synthesis and decomposition of  $\text{AlH}_3$ ”, NANOMAT conference, Lillehammer, June 2009.
35. H. Grove, M.H. Sørby, L.H. Rude, T.R. Jensen, B.C. Hauback, “Substituting  $\text{BH}_4$  with halide in  $\text{Ca}(\text{BH}_4)_2$ ”, 6<sup>th</sup> Nordic Center of Excellent on Hydrogen Storage Materials meeting, Vilnius, Lithuania, October 2009
36. Torben Jensen, “Synthesis of borohydrides and structural diversity“, Hydrogen Storage Materials (HN2), Task-22 IEA HIA Expert Meeting, Paris, France, October 11-15, 2009.
37. Martin Dornheim, “Reaction mechanism and kinetics of  $\text{MgH}_2$ /borohydrides based Reactive Hydride Composites “, 11<sup>th</sup> International Conference on Advanced Materials (ICAM 2009), Rio de Janeiro, Brazil 2009

38. M.Baricco, “Experimental and theoretical studies on hydrogen storage materials”, IEA HIA TASK 22 Meeting, Fundamental and applied hydrogen storage materials development, April 11 - 15, 2010 Death Valley, California
39. M. Baricco, M. Palumbo, E. Pinatel, M. Corno, P. Ugliengo. "Thermodynamic Database for Hydrogen Storage Materials", CIMTEC 2010, 5th Forum on New Materials, Symposium Fb, Materials and Process Innovations in Hydrogen Production and Storage, Montecatini Terme, June, 13-18, 2010)
40. K. Taube, M. Dornheim, “Reaction mechanism and kinetics of  $\text{MgH}_2$ /borohydride based reactive hydride composites“, First International Conference on Materials for Energy, Karlsruhe, July 4 – 8, 2010, [www.dechema.de/enmat2010](http://www.dechema.de/enmat2010)
41. Hauback, B.C., Llamas-Jansa, I., Aliouane, N., Deledda, S., Fonnelløp, J.E., Frommen, C., Grove, H., Lieutenant, K., Sartori, S., Sørby, M.H.:  $\text{BH}_4^-$  substituted by  $\text{Cl}^-$  in  $\text{NaBH}_4$ . MH2010, 12<sup>th</sup> International Symposium “Metal-Hydrogen Systems - Fundamentals and Applications”, Moscow, July, 19-23 2010)

### Posters:

1. Line Rude, Bo Richter, Yaroslav Filinchuk, Magnus H. Sørby, Bjørn C. Hauback, Torben R. Jensen, Anion substitution, „Tuning the stability of  $\text{Ca}(\text{BH}_4)_2$  by substitution of  $\text{CaI}_2$ “, 39th Danish Crystallographers Meeting and 2nd DANSCATT Meeting, Copenhagen, Denmark, June 2-3, 2009
2. Dorthe Ravnsbæk, Yaroslav Filinchuk, Yngve Cerenius, Jørgen Skibsted, Torben R. Jensen, „Mixed-metal boron-based hydrides as potential future hydrogen storage materials“, SMEC2009 study of matter at extreme conditions, Miami - Western Caribbean. March 28 - April 2, 2009
3. Klaus Taube, Martin Dornheim, José Bellosta von Colbe, Rapee Goslawit, R. Bormann, Bjørn Hauback, Hilde Grove, Magnus Sørby, Jon Erling Fonnelløp, Jiri Muller, Lene Mosegard, Torben R. Jensen, Line Rude, Bo Richter, Marcello Baricco, Marta Corno, Pablo Arnal, José Ramallo Lopez, George Kaplanis, George Lagios, “FLYHY - Fluorine Substituted High Capacity Hydrides for Hydrogen Storage at Low Working Temperatures”, Gordon Research Conference on “Hydrogen-Metal Systems”, Lucca / Barga, Italy, July 12 – 17., 2009
4. J. Bellosta von Colbe, R. Goslawit, M. Dornheim, “Fluorine Substitution in Complex Hydrides as Hydrogen Storage Materials”, Gordon Research Conference on “Hydrogen-Metal Systems”, Lucca / Barga, Italy, July 12 – 17, 2009
5. J.E. Fonnelløp, S. Sartori, B.C. Hauback: “Effect of fluoride additives on the decomposition of alane”, Gordon Research Conference on “Hydrogen-Metal Systems”, Lucca / Barga, Italy, July 12 – 17, 2009
6. Dorthe Ravnsbæk, Yaroslav Filinchuk, Yngve Cerenius, Jørgen Skibsted, Torben R. Jensen, “Mixed-metal boron-based hydrides as potential future hydrogen storage materials“, Gordon Research Conference on “Hydrogen-Metal Systems”, Lucca / Barga, Italy, July 12 – 17, 2009
7. José M. Ramallo-López, Félix G. Requejo, Karina Suárez Alcántara, Ivan Saldan, José M. Bellosta von Colbe, Martin Dornheim, Torben R. Jensen, Bo Richter, Line H. Rude, José Avila, María Carmen Asensio, “Boron K-edge NEXAFS Study Of Novel Hydrogen Storage Materials”, 4<sup>th</sup> SOLEIL Users' Meeting, January 21st & 22nd, 2010, École Polytechnique – Palaiseau, Paris, France
8. Marta Corno, Eugenio Pinatel, Piero Ugliengo and Marcello Baricco; "Thermodynamic properties of  $\text{AlH}_3/\text{AlF}_3$  and  $\text{MgH}_2/\text{MgF}_2$  systems as hydrogen storage materials: A computational approach", 4th Symposium Hydrogen& Energy, Wildhaus, Switzerland, January, 24-29, 2010)

9. E. Pinatel, M. Corno, P. Ugliengo and M. Baricco; "Thermodynamic description of hydride-fluoride mixtures for hydrogen storage", Third World Round Robin Seminar WRRS 2010 "PHASE DIAGRAMS FOR ENERGY SAVING", Montpellier, March, 21-23, 2010)
10. I.Saldan, J.Bellosta von Colbe, K.Suarez, R.Gosalawit, C.Pistidda, U.Bösenberg, M.Schulze, T.Klassen, T.Jensen, Y.Cerenius, K.Taube, M.Dornheim, "Possible fluorine substitution for H atoms in Li[BH<sub>4</sub>] and LiH during hydrogen absorption/desorption", MH2010, 12<sup>th</sup> International Symposium "Metal-Hydrogen Systems - Fundamentals and Applications", Moscow., July, 19-23, 2010
11. M. Corno, E. Pinatel, P. Ugliengo, M. Baricco, "A computational study of thermodynamic properties of M-H-F systems for hydrogen storage applications", MH2010, 12<sup>th</sup> International Symposium "Metal-Hydrogen Systems - Fundamentals and Applications", Moscow, July, 19-23 2010
12. Hino, S; Fonneløp, J.E; Sørby, M.H.; Hauback, B.C: In situ synchrotron diffraction studies of halide substitution in Mg(BH<sub>4</sub>)<sub>2</sub>. ERICE 2011 (44th crystallographic course at Ettore Majorana Centre, Erice), Italy
13. Olena Zavorotynska, Marta Corno, Piero Ugliengo, Giuseppe Spoto, Line H. Rude, Lene M. Arnbjerg, Torben R. Jensen, Marcello Baricco, "Mid-infrared, powder diffraction and *ab initio* study of Anion substitution in LiBH<sub>4</sub>", 44th course in International School of Crystallography "The Power of Powder Diffraction," June 2-12, 2011, Erice, Italy
14. Line H. Rude, *Hydrogen storage - saving the energy*, iNANO Annual meeting 18<sup>th</sup> of January 2012, Aarhus University, Aarhus, Denmark
15. Line H. Rude, Yaroslav Filinchuk, Yngve Cerenius, Torben R. Jensen, *Visualisation of Anion substitution by in situ SR-PXD*, Maxlab Annual meeting, 14<sup>th</sup> of November 2011, Lund, Sweden
16. Line H.Rude, S. Hino, O. Zaravotynska, Torben R. Jensen, *Improving hydrogen storage materials by fluoride substitution*, Inano Autumn School 7-10<sup>th</sup> of october 2011 Fuglsøcenteret, Danmark
17. Line H. Rude, Yaroslav Filinchuk, Torben R. Jensen, *Improving the reversibility of LiBH<sub>4</sub> - The LiBH<sub>4</sub>-LiI system*, iNANO Annual Meeting 19<sup>th</sup> of January 2011, Aarhus University, Aarhus, Denmark
18. Line H. Rude, Y.Filinchuk and T.R.Jensen, Anion substitution in Ca(BH<sub>4</sub>)<sub>2</sub>-CaI<sub>2</sub>, *The structure of three new compounds*, 40th Danish Crystallography and 3rd DanScatt meeting, 31<sup>st</sup> of May to 1<sup>st</sup> of June 2010, Copenhagen, Denmark
19. Line Rude, Lene M. Arnbjerg, Yaroslav Filinchuk, Hilde Grove, Yngve Cerenius, Bjørn C. Hauback, Torben Jensen Anion substitution. Tuning the hydrogen release temperature of hydrogen storage materials, iNANO annual meeting 20th of January 2010, Aarhus University, Aarhus, Denmark
20. Marta Corno, Eugenio Pinatel, Piero Ugliengo e Marcello Baricco *Ab-initio modelling of the halide substitution in simple metal hydrides and borohydrides as hydrogen storage candidates* Gordon Research Conference "Hydrogen-Metal Systems" - A Cross-Disciplinary View of Hydrogen Interactions, Easton MA (17-22 July 2011) "
21. C. Pistidda, K. Suarez Alcantára, F. Karimi, C. Bonatto Minella, L. Rude, J. Bellosta von Colbe, K. Taube, T. R. Jensen, T. Klassen, M. Dornheim, "Hydrogen Sorption Properties of the MgB<sub>2</sub> based CaH<sub>2</sub> and CaH<sub>2</sub>-CaF<sub>2</sub> Reactive Hydride Composites", 6<sup>th</sup> Empa Symposium Hydrogen & Energy, Stoops, Switzerland, 22-27. Januar 2012

### Participations at fairs

- Hanover Trade Fair, Group Exhibit Hydrogen and Fuel Cells, April 2009 (TROPICAL)



- WHEC 2010, World Hydrogen Energy Conference, Essen, Germany, May 2010
- Hanover Trade Fair, Group Exhibit Hydrogen and Fuel Cells, April 2011 (TROPICAL)
- H2Expo, Hamburg, June 8./9. 2011 (HZG)

#### 4.1.9 Address of the project public website, if applicable as well as relevant contact details.

<http://www.flyhy.eu>



##### Helmholtz-Zentrum Geesthacht

Dr. Klaus Taube  
Max-Planck-Straße 1  
D-21502 Geesthacht  
Germany  
Phone: +49 4152 87 25 41  
Fax: +49 4152 87 26 36  
[klaus.taube@hzg.de](mailto:klaus.taube@hzg.de)  
<http://hydrogen.hzg.de>



##### Institutt for Energiteknikk

Prof. Bjørn Hauback  
P.O. Box 40  
NO-2027 Kjeller  
Norway  
Phone: +47 (63) 80 60 78  
Fax: +47 (63) 81 63 56  
[bjorn.hauback@ife.no](mailto:bjorn.hauback@ife.no)  
<http://www.ife.no>



##### Aarhus Universitet

Prof. Torben René Jensen  
Langelandsgade 140  
DK-8000 Aarhus C  
Denmark  
Phone: +45 (8942) 3894  
Fax: +45 (8619) 6199  
[trj@chem.au.dk](mailto:trj@chem.au.dk)  
<http://www.chem.au.dk/~webuorg/>



##### Università degli Studi di Torino



Prof. Marcello Baricco  
Via Pietro Giura, 9  
I-10125 Torino

Italy  
Phone: +39 (011) 670 7569  
Fax: +39 (011) 670 7855  
[marcello.baricco@unito.it](mailto:marcello.baricco@unito.it)  
<http://www.nis.unito.it>

*Consejo Nacional de Investigaciones Científicas y Técnicas, Instituto de Investigaciones Físicoquímicas Teóricas y Aplicadas INIFTA*

Dr. José Martín Ramallo López  
Sucursal 4 - Casilla de Correo 16  
1900 La Plata  
Argentina  
Phone: +54 (221) 425-7291  
Fax: +54 (221) 425-4642  
[ramallo@inifta.unlp.edu.ar](mailto:ramallo@inifta.unlp.edu.ar)  
<http://www.inifta.unlp.edu.ar/english/requejo.htm>



*Tropical S.A.*

Mr. George Kaplanis  
17 Krokeon Str  
10442 Athens  
Greece  
Phone: +30 (210) 578 54 55  
Fax: +30 (210) 578 54 57  
[info@tropical.gr](mailto:info@tropical.gr)  
<http://www.tropical.gr>

