

FLYHY – Fluorine Substituted High Capacity Hydrides for Hydrogen Storage at Low Working Temperatures – Summary of 1st Reporting Period

Contract No. 226943

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<http://www.flyhy.eu>

OBJECTIVES

At present there is **no hydrogen storage system available fulfilling all requirements for use especially in mobile applications**: 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 focuses 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 behaviour and thermal conductivity of selected compounds,
- (iv) **scaling-up materials production** and doing first tests in a **prototype tank** together with a HT PEM fuel cell.

Tailoring of physical properties such as thermodynamics, i.e. working temperatures, and reaction kinetics, is 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. We have chosen the most electronegative element, fluorine, as the focus of this research project and also its group members in the periodic table, chlorine, bromine and iodine. By partially substituting halogens for hydrogen or functional groups like $(\text{BH}_4)^-$, the enthalpy of reaction of too stable and too unstable high capacity hydrogen storage materials is to be changed to the desired range of -30 to -40 kJ/(mol H_2), while retaining as much hydrogen storage capacity as possible.

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

- **Alane** (AlH_3 , 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_4 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% ($\text{LiBH}_4 + \text{MgH}_2$)) 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 are 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.

RESULTS

For modified alane and RHCs, high energy ball milling routes have been employed, whereas for pure and modified stable and unstable borohydrides several wet chemical routes as well as combinations with reactive ball milling have been developed.

Alane

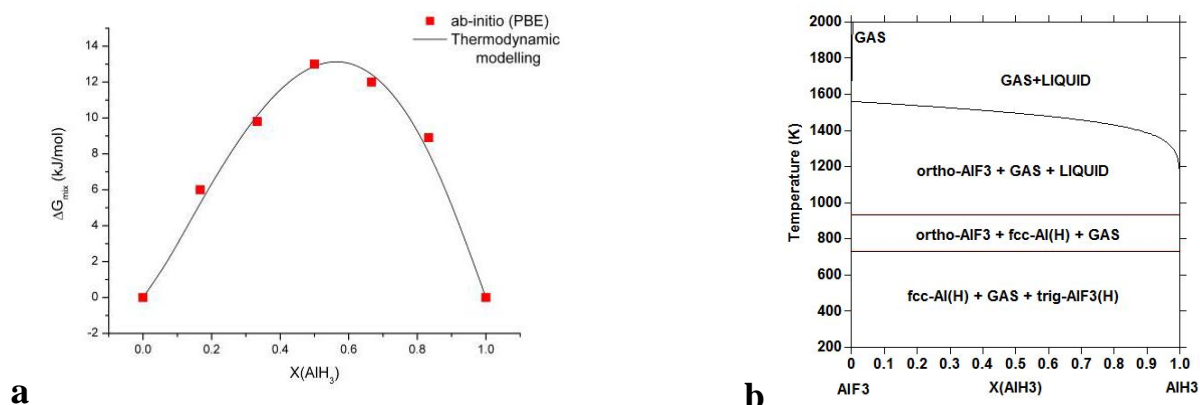


Figure 1: (a) Calculated free energy of mixing of the trigonal solid solution at 298 K and 1bar: first-principles calculations (points) and thermodynamic modelling (line); (b) AlH_3 - AlF_3 pseudo-binary phase diagram.

A wide range of materials compositions and milling parameters were studied, but no indications for fluorine substitution in alane were observed. This is in agreement with our theoretical calculations, which show, that due to a positive enthalpy of mixing of AlH_3 and AlF_3 , fluorine substitution is rather unlikely to occur¹.

¹ J.E. Fonnelløp, M. Sørby, H. Grove, M. Corno, E. Pinatel, P. Ugliengo, M. Baricco and B.C. Hauback, "Experimental and computational investigations on the $\text{AlH}_3 / \text{AlF}_3$ system", Journal of Alloys and Compounds 509 (2011) 10-14, DOI: [10.1016/j.jallcom.2010.08.147](https://doi.org/10.1016/j.jallcom.2010.08.147), \Rightarrow Open Access <http://www.flyhy.eu/publications.html#IFE>

Borohydrides

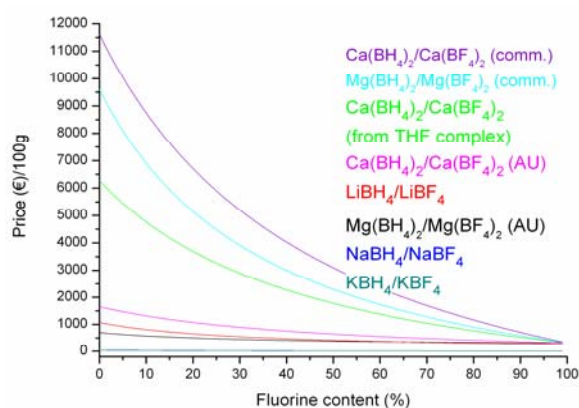


Figure 2: Materials costs for borohydride and tetrafluoroborate mixtures at 100 g of a selected material for a given F/H ratio. Notice that $Mg(BF_4)_2$ is not available as a commercial product, thus the costs of $Mg(BH_4)_2/Mg(BF_4)_2$ are estimated using the price of $Ca(BF_4)_2$. (comm.) = commercial source. (AU) = synthesised at Aarhus University.

addition of fluorine has significant effects on the stability of borohydrides (c.f. Figure 3). up to now many indications for fluorine substitution are observed, e.g. *in situ* PXD and NEXAFS data, but no conclusive structural evidence for substitution of fluorine for hydrogen or $(BH_4)^-$ was found, neither in borohydrides, nor in Reactive Hydride Composites, studied by *in situ* PXD and IR spectroscopy.

Reactive Hydride Composites

The effects of fluorine addition were also studied in RHCs, based on Li, Na and Ca. Effects of fluorine were found in all 3 systems, as shown by changes in hydrogen sorption behaviour e.g. lower hydrogen desorption temperature or significantly increased reaction rates, also double peaks in DSC and changes in boron environment (NEXAFS), all which hint to some structural change. These effects were especially significant in fluorinated composites based on $Ca(BH_4)_2 / MgH_2$.

As shown in Figure 4, by cycling of fluorine containing Ca-based RHC, the onset of hydrogen desorption could be lowered from ca. 300°C down to less than 250°C, while retaining a hydrogen capacity of ca. 7 wt%. Furthermore, modelling of the reaction kinetics (Kissinger method) suggested

For pure, stable borohydrides like $LiBH_4$, $Mg(BH_4)_2$ and $Ca(BH_4)_2$ new wet chemical synthesis methods with high yield have been developed, which not only are significantly cheaper than buying these materials from fine chemicals suppliers (c.f. Figure 2), but have the potential for further cost reduction, as they allow for use of less pure reactants.

The effects of substitution by halogens F, Cl, Br, and I, were studied in selected Li, Na, and Ca-based borohydride systems. For the halogens, Cl, Br, and I, substitution of BH_4^- groups in pure lithium borohydride was found, whereas the calcium borohydride showed only substitution by Cl and I. Substitution with the heavier halogens leads to the stabilisation of the hexagonal high temperature polymorph, *h*- $LiBH_4$, down to room temperature². The substitution is generally observed as a solid solution with the compound containing the larger anion as the host-structure, e.g. formation of CaI_2 type $Ca(BH_4)_{1.3}I_{0.7}$ ³. Also

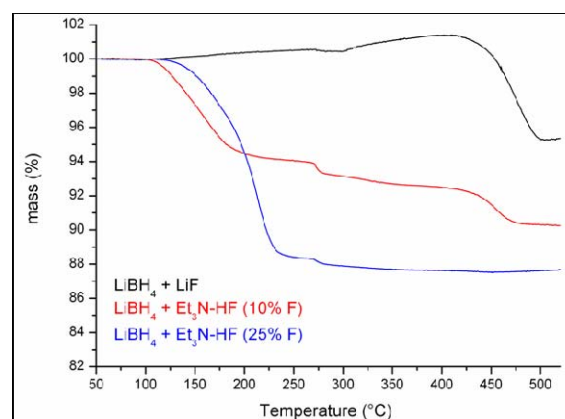


Figure 3: Thermogravimetric (TG) curves for pure *o*- $LiBH_4$ mixed with LiF and two samples of fluorine substituted $LiBH_4$ with 10 and 25 % fluorine. A drastic decrease in desorption temperatures is observed, corresponding with fluorine content.

² Lene Mosegaard, Dorthe Ravnsbæk, Yaroslav Filinchuk, Ronnie T. Vang, Yngve Cerenius, Flemming Besenbacher, Jens-Erik Jørgensen, Hans Jørgen Jacobsen, and Torben R. Jensen, Structure and dynamics for $LiBH_4 - LiCl$ solid solutions, Chem. Mater., 2009, 21, 5772-5782. DOI: [10.1021/cm902013k](https://doi.org/10.1021/cm902013k), ⇒ Open Access <http://www.flyhy.eu/publications.html#AU>

³ Line H. Rude, Yaroslav Filinchuk, Magnus H. Sørby, Bjørn C. Hauback, Flemming Besenbacher, Torben R. Jensen, Anion substitution in $Ca(BH_4)_2-CaI_2$: Synthesis, structure and stability of three new compounds, 2010, submitted

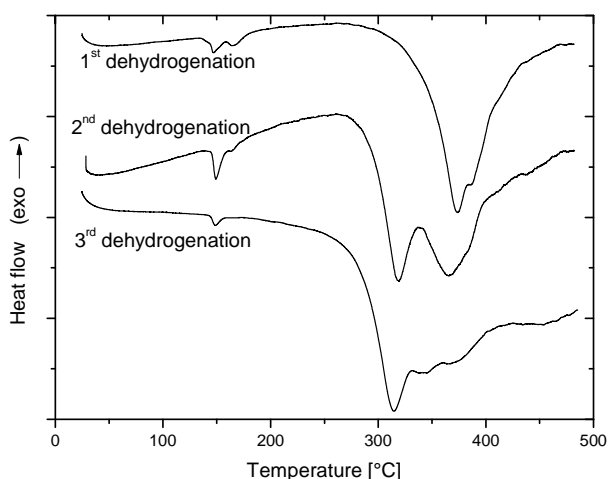


Figure 4: DSC signal of hydrogenated Ca-based RHC, measured at 5 K min^{-1} . The onset of hydrogen release decreased over 3 cycles from ca. 300°C to below 250°C .

a reduction of the activation energy from 160 down to ca. $115 \text{ kJ}/(\text{mol H}_2)$ upon cycling.

CONCLUSIONS AND PERSPECTIVES

The analysis of the various methods for materials synthesis and cost for raw materials show, that on the one hand cost for the storage materials themselves and following cost for purchase of a storage tank based on these are very high, when compared to compressed gas storage. On the other hand, complete life cycle cost of tanks based on these materials will be significantly lower as compressed or liquid hydrogen storage, due to much lower cost for hydrogen processing (e.g. energy consumption for compression).

Based on the experimental and theoretical findings of the 1st period of FLYHY, the

consortium took the following decisions for the 2nd period:

- Work on fluorine substitution in Alane is stopped.
- More detailed structural analysis, e.g. by NEXAFS at the F, B, Ca and Li edges, and in parallel IR, Raman and *in situ* PXD studies will be performed, to clarify the chemical and structural changes in pure borohydrides and RHC, resulting from fluorine addition to the materials, and the function of fluorine in reducing the stability of the borohydrides group and the hydrogen desorption temperatures. Finalizing investigation of not fully understood effects in Li-based RHC.
- Continuation of the investigation of general, cost effective synthesis strategies for fluorine substituted borohydrides.
- Detailed kinetic and thermodynamic studies of the most promising anion substituted systems.
- The prototype tank will be a simple construction based on a design already in use at GKSS. TROPICAL will integrate this in a HT PEM fuel cell test bench..
- As most promising candidates (hydrogen sorption properties, cost for materials synthesis) for scale-up of materials production and testing in a prototype tank in conjunction of a HT PEM FC, (i) physical mixtures of Ca- and Li-based borohydrides with corresponding borofluorides, which exhibit partial reversibility at very low temperatures $< 200^\circ\text{C}$, but release some HF and other compounds, and (ii) Ca-based, F added RHCs, which release hydrogen at ca. 250°C or below, and so far show good cycling stability, were selected. Next steps here will be synthesis of larger amounts of the materials, studying their sorption behaviour as well as compaction and thermal conductivity, for producing a material suitable for filling the prototype tank.

Provided, that a further reduction of hydrogen release temperature and/or cycling stability of the materials, mentioned in the last bullet, can be achieved, FLYHY will develop and demonstrate a hydrogen storage material with a capacities of $\geq 6\text{wt}\%$, and ca. $70 \text{ kg H}_2 / \text{m}^3$ resp., and prototype tank based on that material, which efficiently works in conjunction with a HT PEM fuel cell.