FLYHY
(226943)

Fluorine substituted High Capacity Hydrides for Hydrogen Storage at Low Working Temperatures

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Dr. Klaus Taube
Helmholtz-Zentrum Geesthacht

FLYHY Partnership

Participant no.	Scientist(s)	Organisation Legal Name	Country	Acronym	Special Tasks
1	**Klaus Taube** **Martin Dornheim** José Bellosta v. Colbe Karina Suarez Alcantará Ivan Saldan	Helmholtz Zentrum Geesthacht	Germany	HZG	RHC, Scale-Up, Tank design, SAXS@BESSY
2	**Björn Hauback** Magnus H. Sørby Jon Erling Fonneløp Hilde Grove	Institutt for Energiteknikk, Kjeller	Norway	IFE	Alane, Borohydrides, Cryomilling, PND@JEEP, PXD@SNBL
3	**Torben Jensen** Bo Richter Line Rude	Aarhus Universitet	Denmark	AU	Borohydrides, wet chemical synthesis, PXD@MAX-Lab, NMR
4	**Marcello Baricco** Piero Ugliengo Marta Corno Olena Zavorotynska Eugenio Pinatel	Università degli Studi di Torino	Italy	UNITO	Theory & Modelling, IR & Raman
5	José Ramallo Lopez Pablo Arnal	CONICET Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, La Plata	Argentina	CONICET	EXAFS, NEXAFS / XANES, XPS
6	**George Kaplanis**	Tropical S.A.	Greece	TROPICAL	Scale-Up, Tank Testing, Techno-Ecomomical Evaluation

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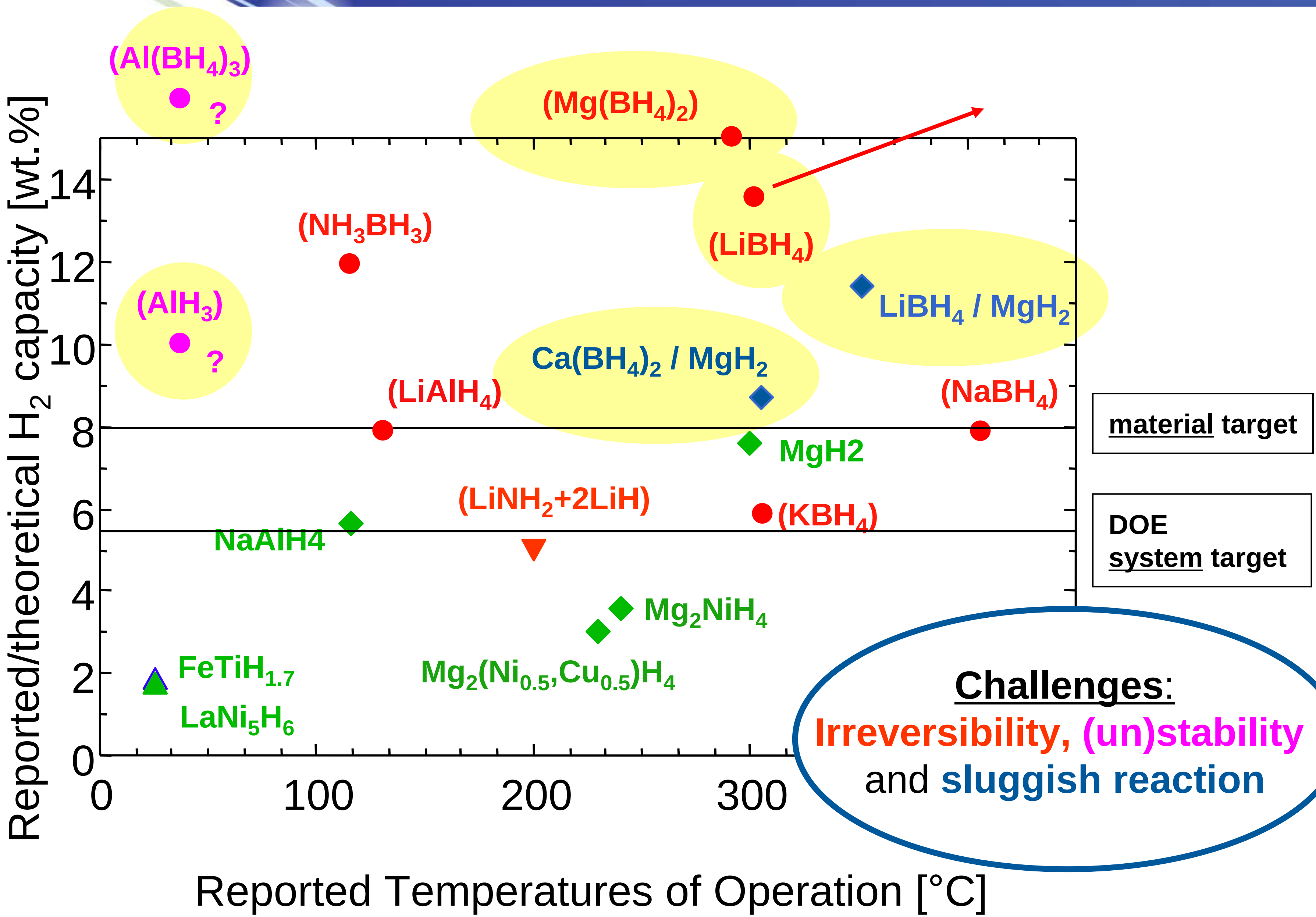
Metal Hydrides for Hydrogen Storage



Challenges:
Irreversibility, (un)stability
and **sluggish reaction**

Targets of FLYHY

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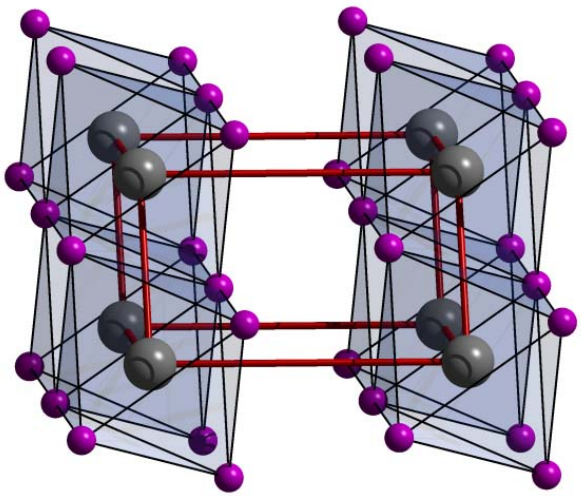
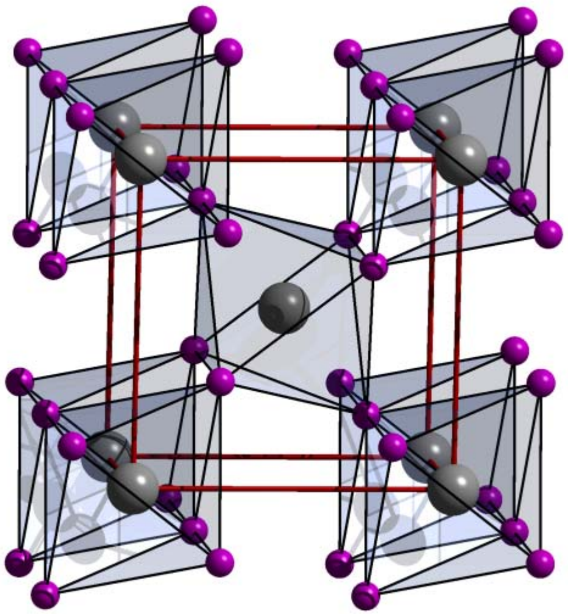
- Investigate the novel approach of **anion substitution by halogens**
  - **Alane, stable and unstable Boron Hydrides, Composites**
- **Scientific understanding** of the chemical and structural changes responsible for the desired properties
- Knowledge-based development of diverse hydrogen storage materials by **advanced computer based modelling** (*ab initio*, CALPHAD, …)
- Detailed **techno-economical evaluation** of solid state storage materials (performance in test tank, cost, benchmarking)
- GO/NO-GO criteria:
  - Materials with > 6 wt.% storage capacity
  - change in $|\Delta H| > 5 – 10$ kJ/(mol H_2) depending on system, and/or
  - significant drop in temperature of reversible loading/unloading while at least retaining sorption kinetics

Heavy Halogens (Cl^-, I^- , Br^-) substituting for $(BH_4)^-$

CaI_2 type structure,
***tri*-$Ca((BH_4)_{0.7}I_{0.3})_2$, *T* = 27 °C**

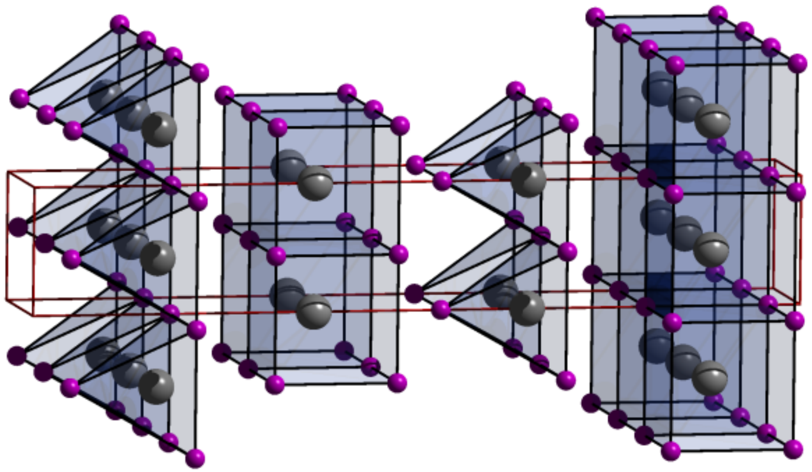




$CaCl_2$ type structure,
***ort*-$Ca((BH_4)_{0.7}I_{0.3})_2$,**
***T* = 180 °C**

***ort*-$Ca((BH_4)_{0.7}I_{0.3})_2$,**
$CaCl_2$ and β-$Ca(BH_4)_2$
are structurally
related

New structure type
***tet*-$Ca((BH_4)_{0.4}I_{0.6})_2$**
***T* = 320 °C**

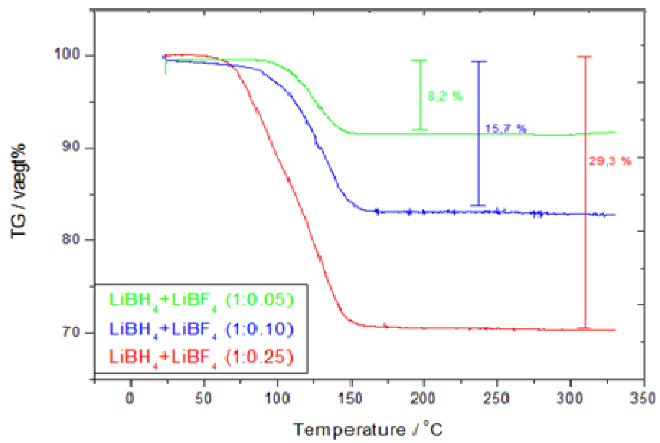


Rude, L.H.; Filinchuk, Y.; Sørby, M.H.; Hauback, B.C.; Besenbacher, F.; Jensen, T.R., J. Phys. Chem. C, 115 (15), (2011) 7768-7777, (DOI: 10.1021/jp111473d)

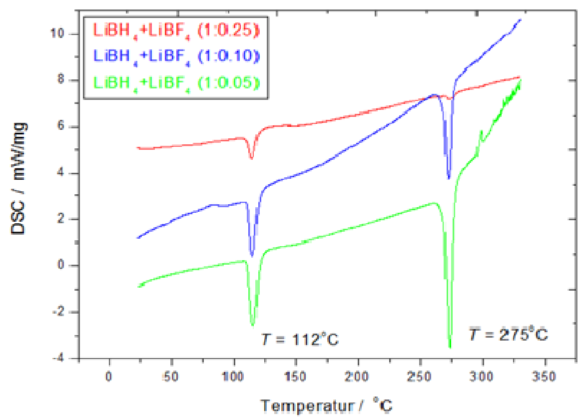
F addition to stable borohydrides

- $M(BH_4)_n$ – $M'(BF_4)_n$ systems:
  - M, M' = Li, Na, K, Mg
- e.g. $LiBH_4$ – $LiBF_4$:
  - >33% molar% $LiBF_4$: new phase
  - <33% molar% $LiBF_4$: **significant mass loss between 70-120°C**

TG



DSC



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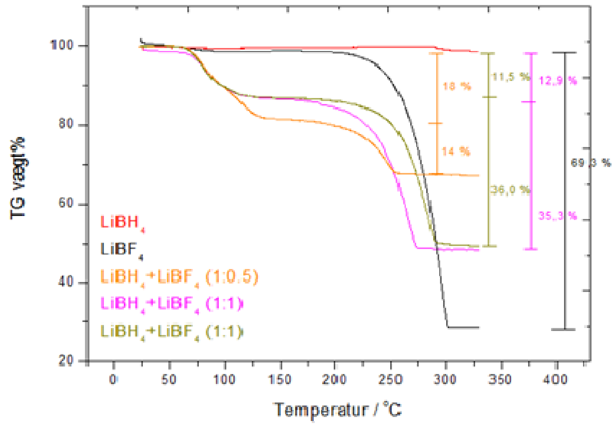
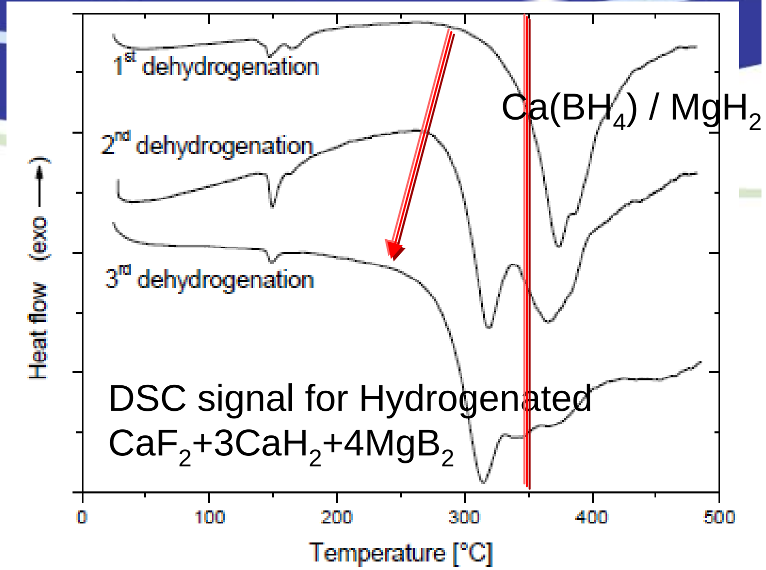


$LiBH_4$ – $LiBF_4$
(1:0.05/1:0.1/1:0.25)

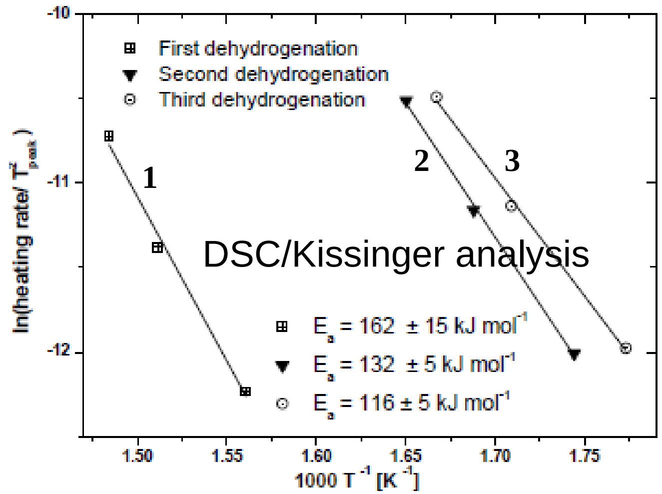
$LiBH_4$ – $LiBF_4$
(1:0.5/1:1)

F addition to Reactive Hydride Composites (RHC)

- Ca-based RHC: most promising
  - ~2x faster reaction rates reasonable H_2 storage capacity.
  - T_{peak} clearly shifted towards lower T
  - $|\Delta H_{dec}|$ lowered by $\geq$ 5 kJ/(mol H_2)
  - More precise PCT measurement needed.

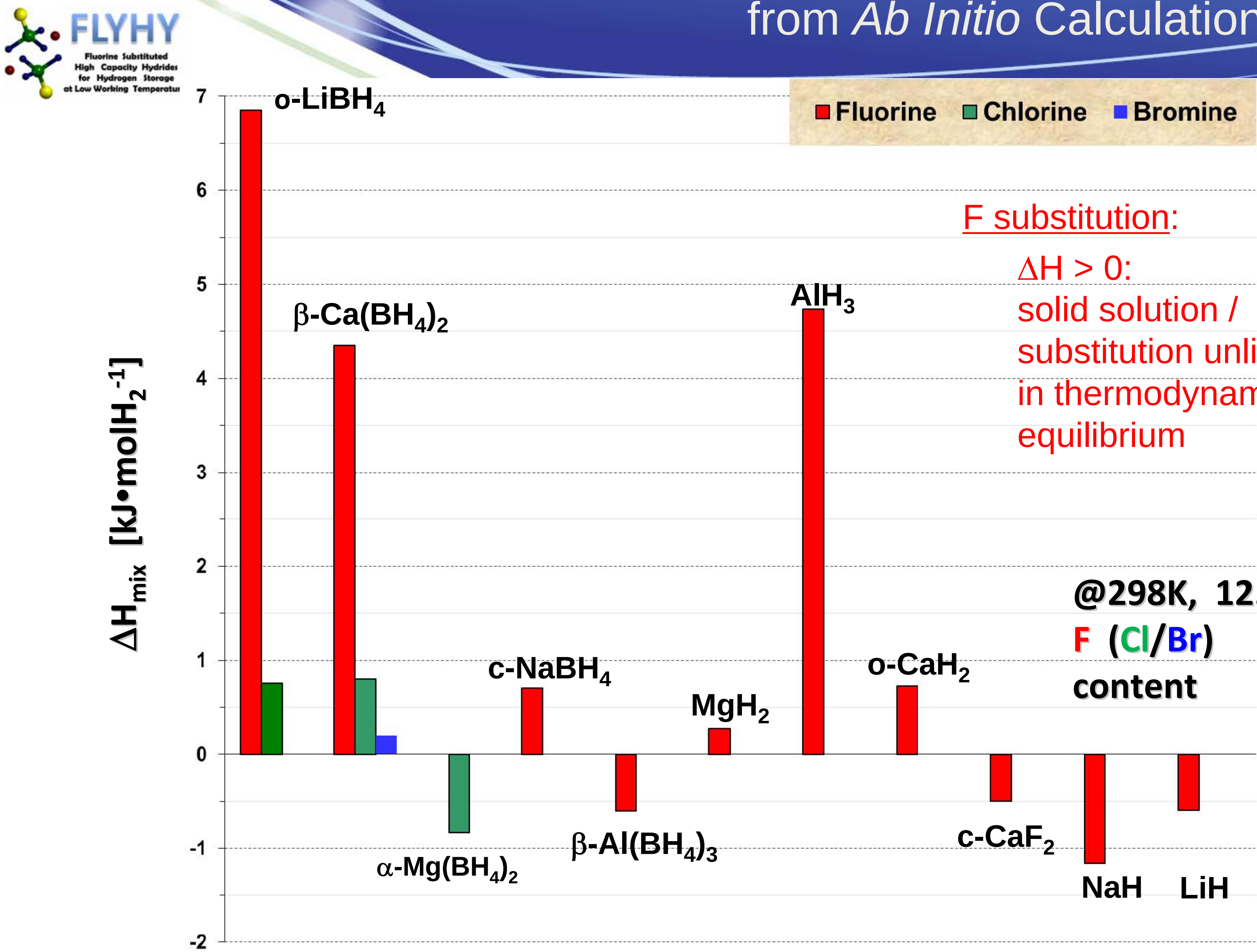


- Significantly reduced activation energy for H_2 release during cycling
- Possibly microstructural refinement



- In situ SR-PXD: a new intermediate may be involved in H_2 release and uptake

Determination of Enthalpies of Mixing from *Ab Initio* Calculations



F substitution:

$\Delta H > 0$:
solid solution / substitution unlikely in thermodynamic equilibrium

@298K, 12.5% F (Cl/Br) content

Benchmarking

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Material system (optimal stoichiometry)	Max. H_2 Capacity	Max. H_2 Capacity	Temperature for Dehydro-geneation	Time for dehydro-genation, back pressure	Reaction Enthalpy	Pressure, Temperature, Time for hydrogenation	Degradation / Improvement upon cycling	Materials cost	Materials cost
	wt.%	kg H_2/m^3	°C	h / bar	kJ / (mol H_2)	bar / °C / h		€ / kg	€ / kg stored H_2
Hydralloy C® (TiCrMn)	1,8	120	RT		~ 20	21 / 40 / -		40 - 100	2.105 - 5.263
$LaNi_5$ (MischMetall based alloy)	1,3	110	RT			3 / RT / -		26 (120 for pure $LaNi_5$)	2.000
$NaAlH_4$ (with Ti additive)	4,5	40	140		~ 40	100 / 130 / 0,15		824 (20)	18.311 (444)
$LiBH_4$ / MgH_2	9	> 90	420	70 / 5	46	50 / 350 / 18		2.136 (40)	23.289 (444)
$Ca(BH_4)_2$ / MgH_2, F substituted	7,6		250 - 300	4 / 0.1		130 / 350 / 3		1.141	15.013

Conventional Technologies	Max. H_2 Capacity	Max. H_2 Capacity	Temperature for Dehydrogeneation	Loss Energy needed for compression or liquefaction	Cost per kg stored H_2
	wt.%	kg H_2/m^3	°C	kJ / (mol H_2)	€ / kg
CHS@350 bar	3.5	18	RT	14,5	
CHS@700 bar	4	25	RT	16,2	1.300 – 4.000
LHS@20K	25	60	Heating necessary	109,4	5.000 – 20.000

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Final Conclusions

- Substitution by Cl, I, Br in pure boron hydrides
  - substitute for complete $(BH_4)^-$ group, new crystalline structures found
  - trend to stabilisation of HT phases
  - help rehydrogenation/reversibility, but do not enhance kinetics
- Substitution with F
  - No F-substituted AlH_3 $\Rightarrow$ confirmed by modelling $\Rightarrow$ **Work stopped**
  - Partly strong destabilisation of pure boron hydrides
    - Decomposition below 200°C (100°C)
    - (Partly) Irreversible release of H and heavier compounds (e.g. diborane)
  - Ca-based RHC most promising system $\Rightarrow$ investigation in test tank
    - H release between 200 and 250°C (compared to 350°C w/o F), no diborane
    - decreased reaction enthalpy ($|\Delta H| > 5$ kJ/mol H_2), significantly enhanced kinetics
    - 100 g of material under test in lab tank together with HT PEM FC
    - Enhancement of kinetics & capacity seem to decrease upon cycling
    - no conclusive evidence for F substituting for H (theory ↯ experiment)
- **Cost!!!!**

Correlation of the project with the targets of the MAIP/AIP

- AA 2: Hydrogen Production, Storage & Distribution
  - MAIP
    - Long-term and break-through oriented research on improved solid .. hydrogen storage options for increased efficiency and storage capability, i.e. 2nd generation hydrogen storage technology.
    - Improved system density for H2 storage (2015: 9 %wt of H2)
  - AIP 2011
    - a portfolio of sustainable hydrogen production, storage and distribution processes: Improved solid state and underground storage
    - Storage materials with capacities ≥ 6 wt.%, ≥ 60 kg H_2/m^3 reversibly releasing hydrogen at operating temperatures compatible e.g. with PEM FC, HT PEM FC or SOFC / MCFC
    - Cost effective production routes of the materials

Project activities related to targets of MAIP/AIP

- Development of novel hydrogen storage materials with capacities > 8 wt.% and 60 kg H_2/m^3
  - Halogen substituted boron hydrides
  - Halogen substituted boron hydride based Reactive Hydride Composites
- Understanding of microstructural changes and reaction upon hydrogen loading and unloading
  - Advanced characterisation (*in situ* PXD, Raman, NEXAFS at low energies)
  - Comprehensive theoretical modelling and assessment
  - Building and testing of a laboratory size prototype tank
- Cost
  - Benchmarking
  - Development of novel cost effective routes for materials synthesis
  - Techno-economical evaluation

Contributions to non-scientific targets

- Training and Education
  - Training of young experts in the field of hydrogen storage materials
    3 PostDoc, 2 PhD positions
    - Basic and advanced characterisation
    - Cost effective materials production
    - Hydrogen storage tank design
- Dissemination & public awareness
  - Publications in scientific and popular journals
  - Presentations at workshops, conferences (e.g. Gordon Research Conference) and fairs (Hanover Fair, H2Expo)
  - Website http://www.flyhy.eu
  - CORDIS Technology Marketplace
    http://cordis.europa.eu/fetch?ACTION=D&SESSION=&DOC=1&TBL=EN_OFFR&RCN=6762&CALLER=OFFR_TM_EN

Technology Transfer / Collaborations

- Partners participated/(-ing) in NESSHY, NANOHY, SSH2S, H2FC, COST
- Japanese HYDROSTARS Programme (Etsuo Akiba, Kyushu University), other Japanese groups (e.g. Shin-ichi Orimo, Tohoku University)
- 5 Scientists from FLYHY experts in IEA HIA Task 22 "Fundamental and applied hydrogen storage materials development“
- FLYHY scientists acting as experts for US DOE on SSHS
- 3 partners members of Working Group “Solid State Hydrogen Storage” inside N.ERGHY
- Interfaces to national organisations
  - Deutscher Wasserstoff und Brennstoffzellen Verband
  - The Danish Partnership for Hydrogen and Fuel Cells
  - The Norwegian Hydrogen Forum
  - Italian Hydrogen Association
  - Hellenic Hydrogen Association

Project Future Perspectives

- Proposed future research approach and relevance
  - FCH JU Call 2011 on SSH2 direct consequence of FLYHY results
    - Novel hydrogen storage materials
    - Materials cost!!! ⇒ synthesis routes, “cheap” raw materials
      ⇒ fundamental research
    - Prototyping of complete application
- Need/opportunities for increasing cooperation
  - European wide research infrastructure on hydrogen technology
  - Support for more fundamental research (e.g. FP7 & FP8) besides FCH JU
  - Support for bridging the gap between fundamental research (e.g. Marie Curie) and industrial application needed
    ⇒ Technology validation projects (Research & industry)
- Need/opportunities for international collaboration
  - Excellent experiences with collaboration with Argentina
  - Top groups world wide should be included (and funded) in projects
- Possible contribution to the future FCH JU Programme
  - c.f. FCH JU Call 2011 on SSH2, MAIP

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Thank you

Questions and Comments welcome

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

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