TAILORING BOROHYDRIDES FOR REVERSIBLE HYDROGEN STORAGE

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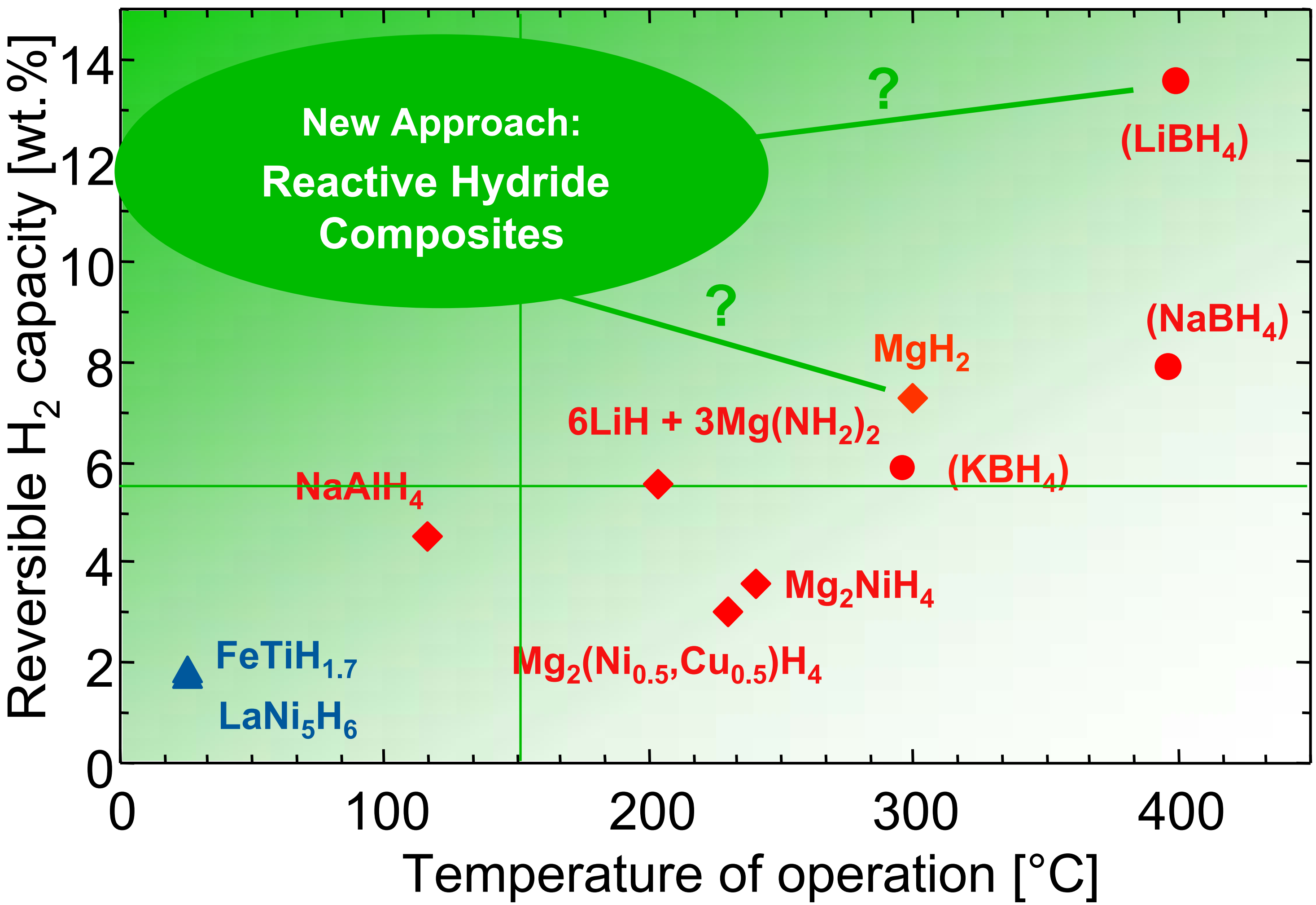
HELMHOLTZ ASSOCIATION

Novel Materials for Solid State Hydrogen Storage



DOE revised **system** target 2015

Reactive Hydride Composites (RHC)

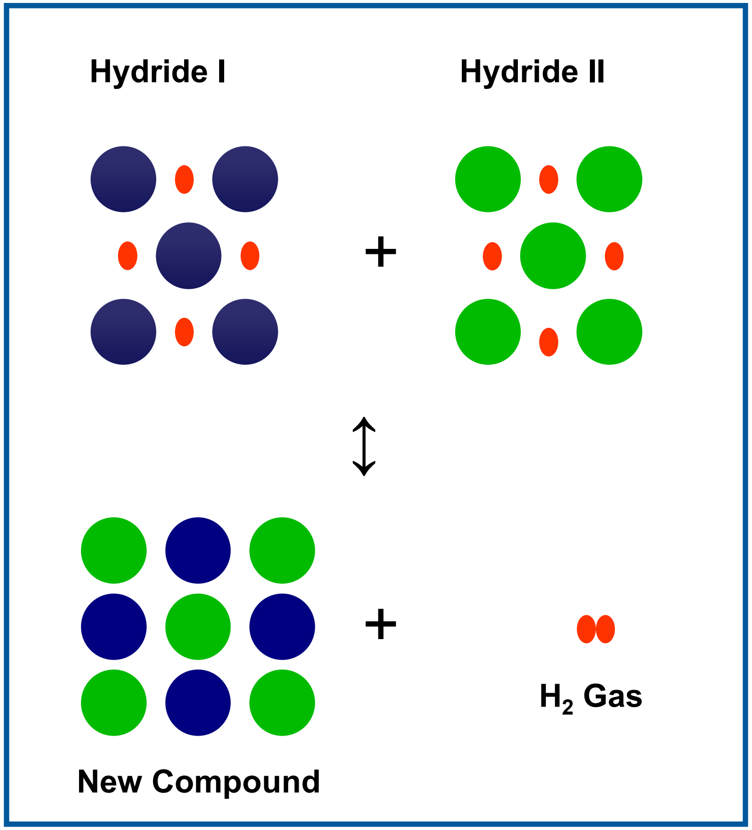
Let's consider two hydrides in a composite

which interact upon desorption

Apply to light-weight hydrides

e.g. MgH_2, alanates, amides

borohydrides ??



G. Barkhordarian et al.: GKSS patent application 2004

J.J. Vajo et al.: GM patent application 2004

Reactive Borohydride Composites

- $MgH_2 + 2\ NaBH_4 \longleftrightarrow MgB_2 + 2\ NaH + 4H_2$ **$\Delta H =$ 63.5 kJ/mol H_2, 7.8 wt.%**
- $MgH_2 + Ca(BH_4)_2 \longleftrightarrow MgB_2 + CaH_2 + 4H_2$ **$\Delta H \approx$ 20 - 30 kJ/mol H_2, 8.3 wt.%**
- $MgH_2 + 2\ LiBH_4 \longleftrightarrow MgB_2 + 2\ LiH + 4H_2$ **$\Delta H =$ 46 kJ/mol H_2, 11.5 wt.%!!**

G. Barkhordarian et al.: GKSS patent application 2004, J. Alloys & Compounds 440 (2006)

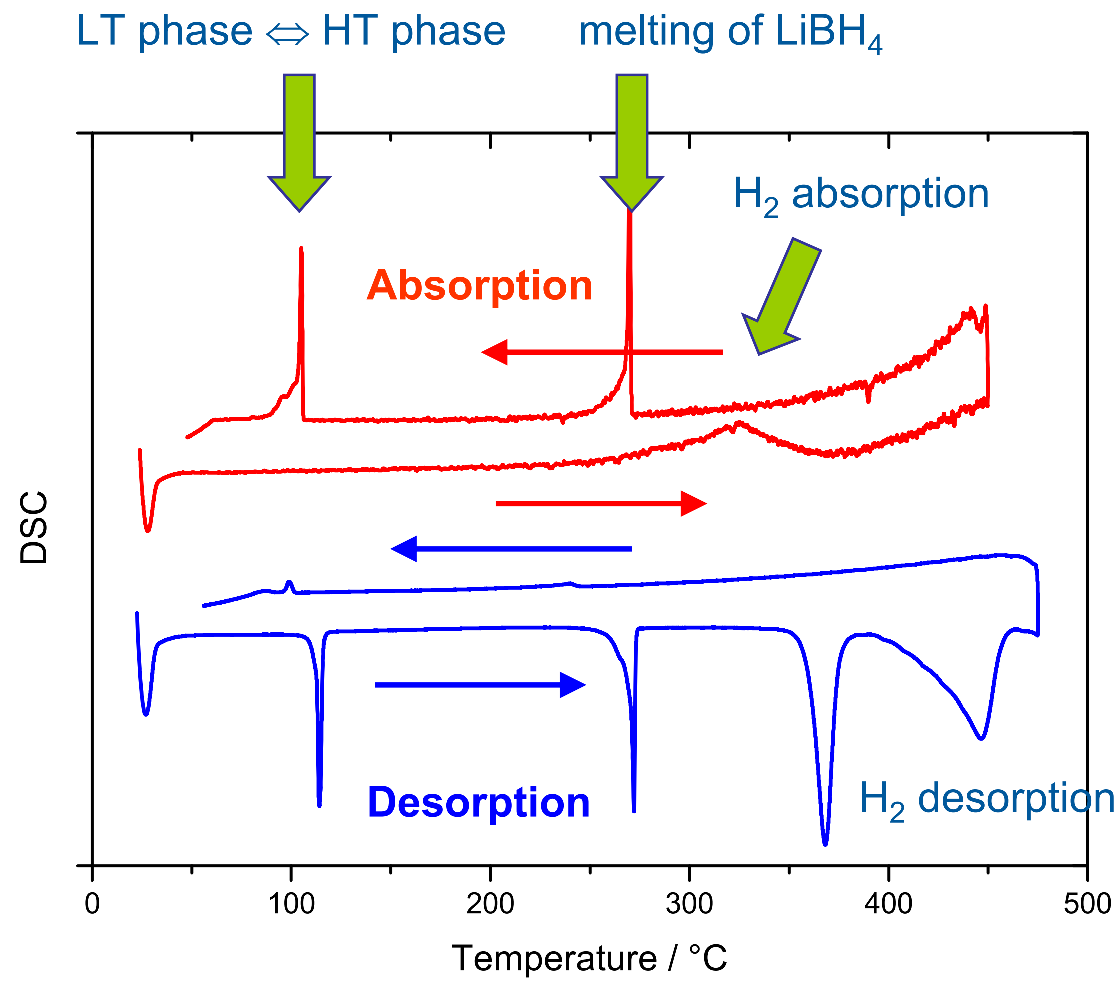
J.J. Vajo et al.: patent application 2004, J. Phys. Chem. B 109 (2005)

Reversibility in $2LiBH_4 + MgH_2$ (w/o cat)

$2\,LiH + MgB_2 + H_2$

50 bar H_2 ↓ ↑ **3 bar H_2**

$2\,LiBH_4 + MgH_2$



M. Dornheim et al., Scripta Materialia 56 (2007)

Reaction Pathway: Desorption
– In-situ XRD measurements –

$LiBH_4$ (LT)+MgH_2

↓

$LiBH_4$(HT)+MgH_2

↓

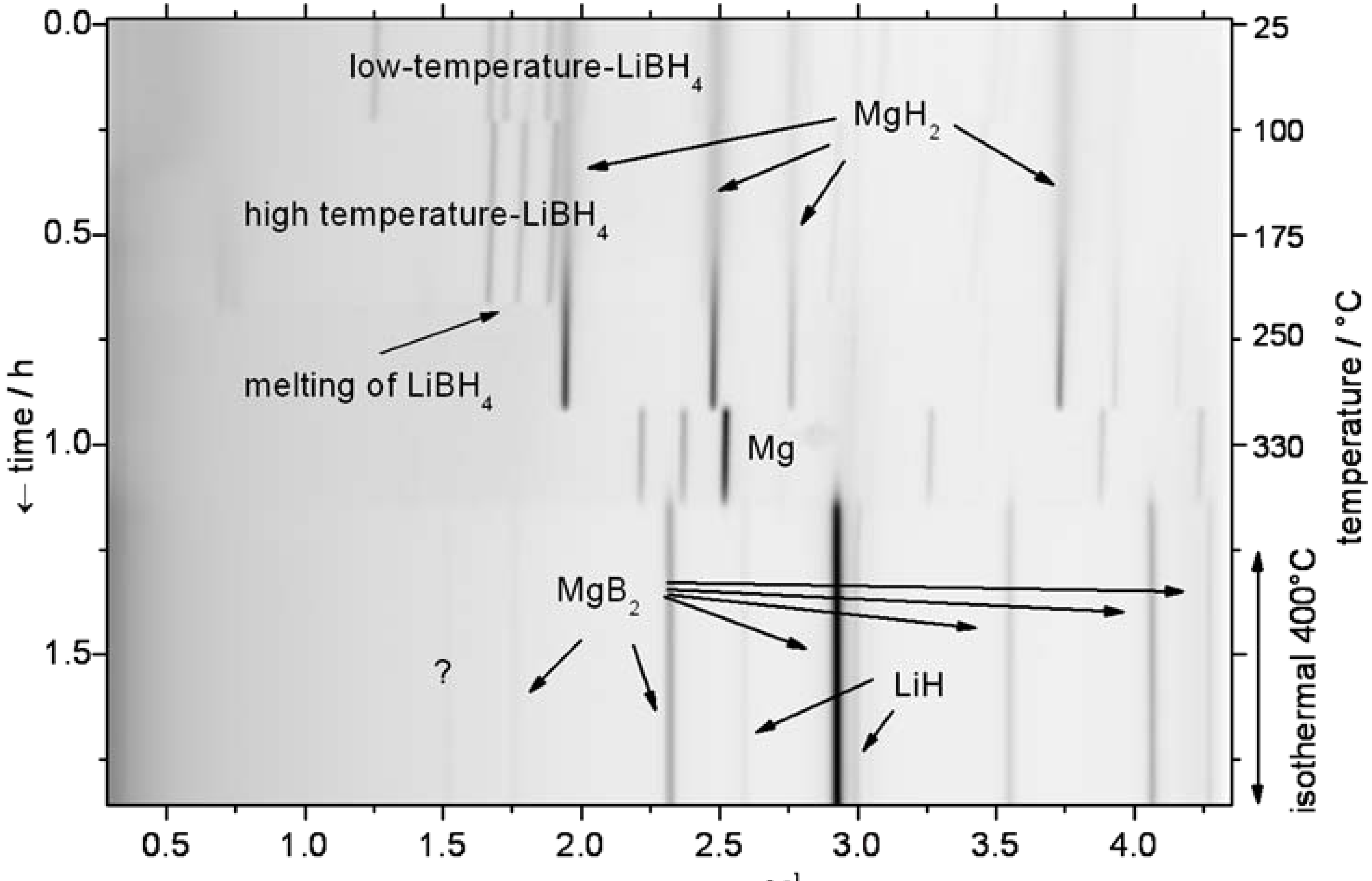
$LiBH_4$(l)+MgH_2

↓

$LiBH_4$(l)+Mg

↓

LiH+MgB_2



U. Bösenberg et al., Acta Materialia 55 (2007)

Measured at I711,

MAX-lab, Lund, Sweden

$2LiBH_4$+MgH_2+5 mol% V-additive

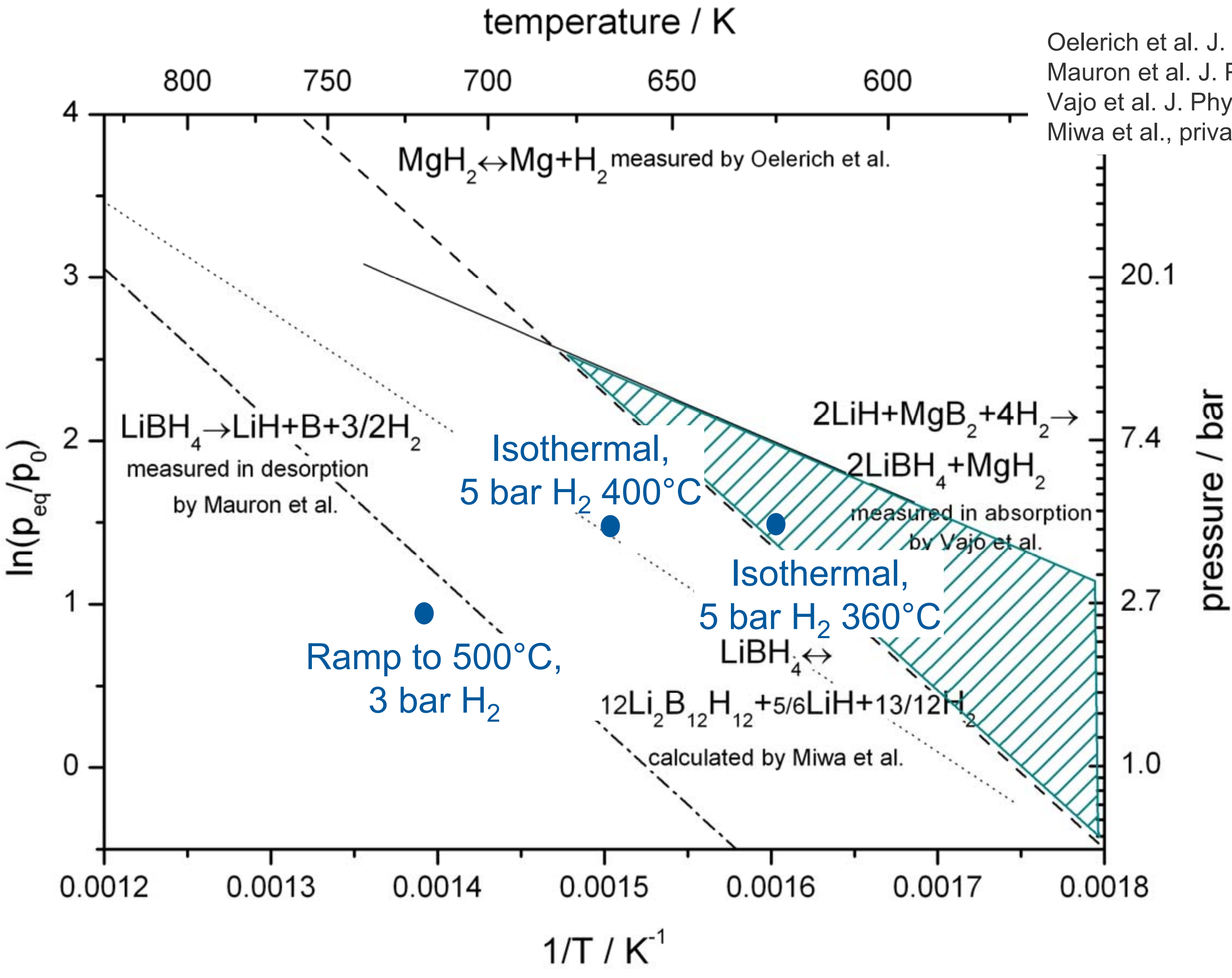
Heating to 400°C, then isothermal, 5 bar H_2-pressure

Features of Reactive Hydride Composites

- at least **two** reacting phases, e.g. MgB_2 and XH
  - → require **homogeneous** and fine-scale distribution of phases
  - → **intermediate phases** may form (e.g. $MgNaH_3$, $Li_2B_{12}H_{12}$)
  - → nucleation problems, slower kinetics (**MgB_2 formation, dissolution**)
  - → might result in **lower reversible hydrogen capacities** with respect to theoretical capacity (known also for NaH + Al)
- (eutectic?) **melting** of borohydride phase
  - → no enhanced kinetics (ionic melt!)
  - → tank design
- complex thermodynamics and kinetics

Van‘t Hoff Plot $LiBH_4$-MgH_2 Composites

Oelerich et al. J. Alloys Compds. (2001) 315:237
Mauron et al. J. Phys. Chem. B (2008)112:906
Vajo et al. J. Phys. Chem. B (2005)109:3719
Miwa et al., private communication 2008



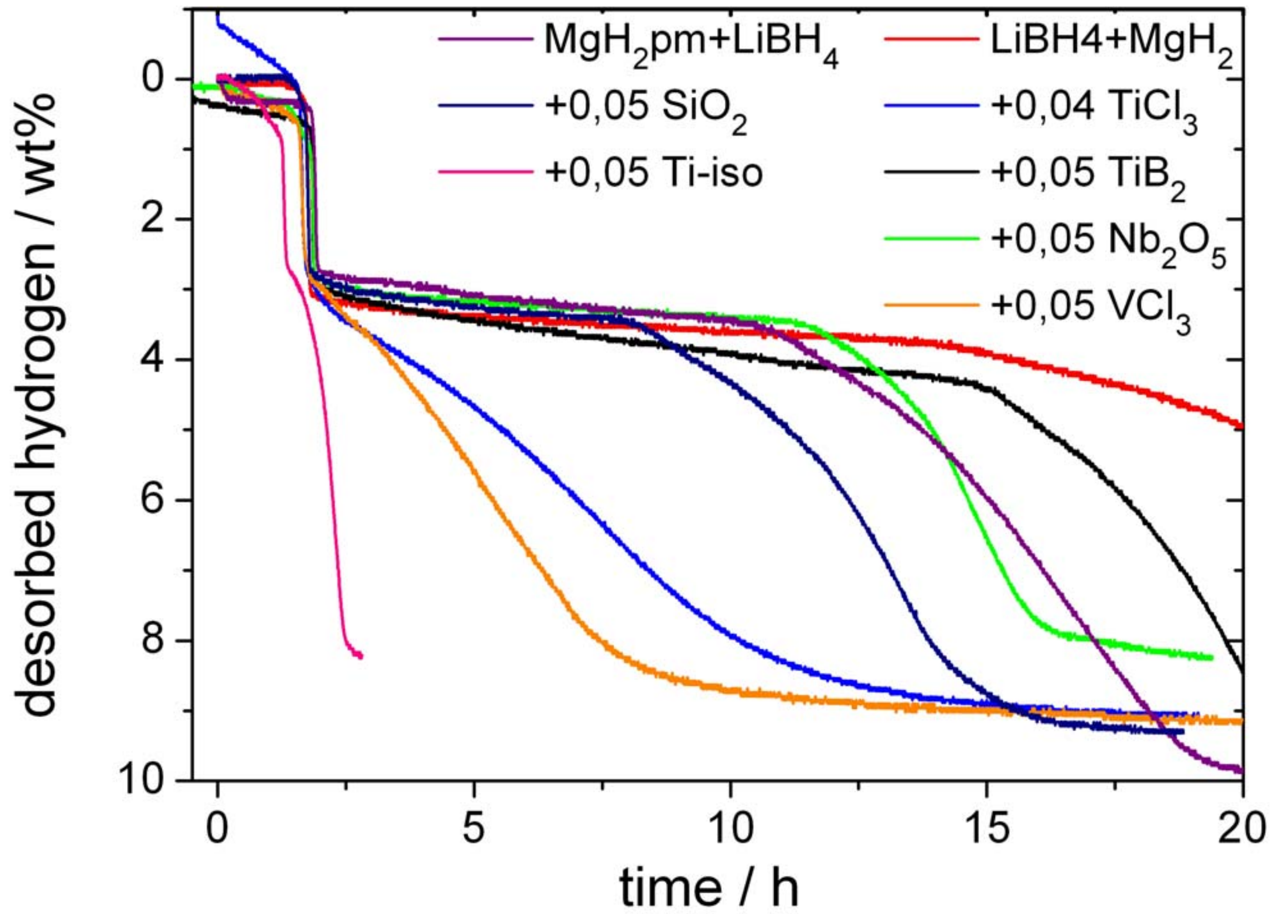
Unique Absorption Kinetics of MgB_2

Target	Composite	Products	H-content (wt%)		
			Calc.	200bar 300°C 48 hr	350bar 400°C 24 hr
$LiBH_4$	LiH+B	No hydride formed	-	-	-
	$2LiH+MgB_2$	$2LiBH_4 + MgH_2$	11.4	8.3	11
	$6LiH+CaB_6$	No hydride formed	-	-	-
	$4LiH+B_4C$	No hydride formed	12.1	-	-
	$Li_7Sn_2+3.5MgB_2$	$7LiBH_4+1.75Mg_2Sn +0.25Sn$	6.3	2.5	3

G. Barkhordarian et al.: J. Alloys & Compounds 440 (2006)

Sorption Kinetics: Desorption

$2\ LiBH_4 + MgH_2 \leftrightarrow 2\ LiH + MgB_2 + 4H_2$ @ T= 400°C, p=5 bar H_2



U. Bösenberg et al., Acta Materialia 55 (2007)

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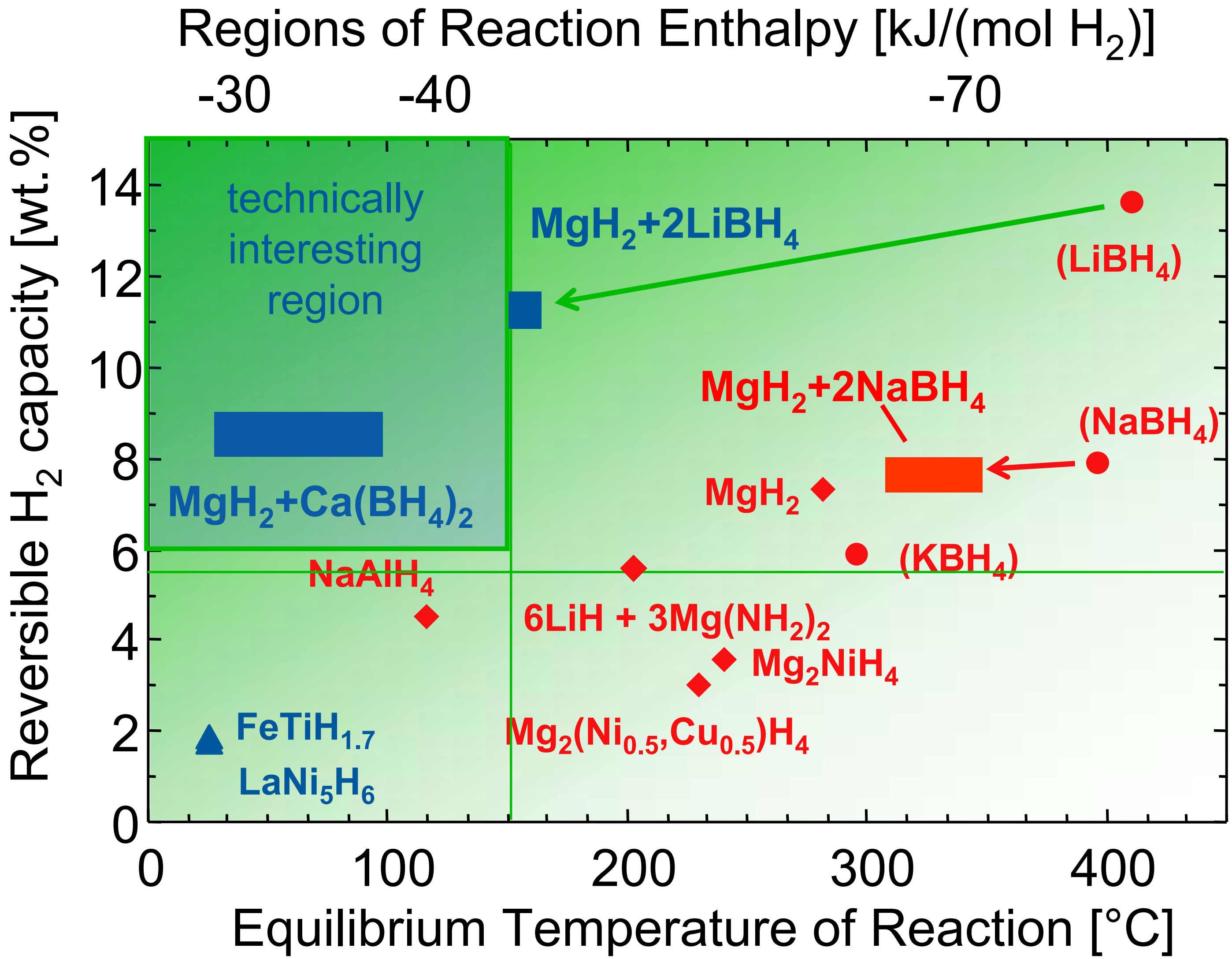

DOE revised system target 2015

Hydrogen Storage Tank of Complex Hydrides

GKSS FORSCHUNGSZENTRUM

(Model) Material: Sodium Alanate $NaAlH_4$

STORHY

- ✓ Gravimetric capacity: 4,5 wt.%
- ✓ Good kinetics, adequate thermodynamics

⇒ **Optimisation** of tank design by

- **Light-weight** construction
- **High capacity** storage materials

Upscaling

0.1g
1x

1g
10x

5g
50x

250g
2500x

8 kg = 400 g H_2
~20 l Tank
for **4500 l H_2**
0,9 wt.%, 22 kg/m^3
80.000x

Conclusions

GKSS FORSCHUNGSZENTRUM

- to tailor borohydrides for reversible hydrogen storage
  RHC is a promising approach (alternatives?)
- complex thermodynamics and kinetics
- kinetics of boron compound formation and dissolution is crucial
- system integration has to consider melting of borohydrides