INITIAL EFFECTS OF COST EFFECTIVE MATERIALS IN $2LiBH_4$-MgH_2 HYDROGEN STORAGE MATERIAL

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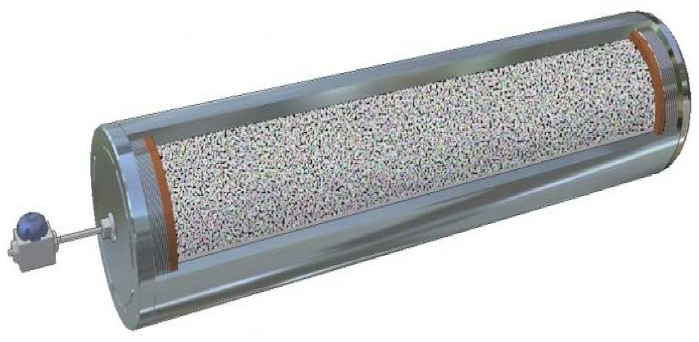
INTRODUCTION

Hydrogen Storage Methods:

- **Gas H_2**: up to 700 bar
- **Liquefied H_2**: -253^{0}C
- **High cost**
- **Safety concerns**



Solid-state storage:
Metal/compounds + H_2 <--->
Hydride/complex compounds

Solid-state Material:

❖ [(1)]**$LiBH_4$: 18.5 wt% H_2, ΔH = -75 kJ/mol H_2, too stable and irreversible due to the formation of boron element, high temperature is required for dehydrogenation (≥ 400 °C)**

$$LiBH_4 \leftrightarrow LiH + \underline{B} + 3/2H_2$$

❖ [(1)]**MgH_2: 7.6 wt% H_2**

$$MgH_2 \leftrightarrow Mg + H2$$

➢ Operate at evaluated temperature, low reaction kinetics (high activation energy, ΔH= -78 kJ/mol H_2)
- Slow diffusion rate
- Insufficient nucleation or poor dissociation of H_2 molecule on material surface

❖ [(1)]**$LiBH_4/MgH_2$: 11.4 wt% H_2 , reversible, ΔH = -46 kJ/mol H_2, $T_m(LiBH_4)$ = 270 °C, T = 265 °C**

➢ Desorption and absorption processes occur at high temperatures with a relatively slow two step kinetic.

$$2LiBH_4 + MgH_2 \rightarrow 2LiBH_4 + Mg + H2 \rightarrow 2LiH + MgB_2 + 4H_2$$

❖ **Improvement in the hydrogen sorption kinetic: Adding additives with catalytic effects (e.g. $TiCl_3$; $3TiCl_3.AlCl_3$);**

➢ Cost: $TiCl_3$ > **4x** ($3TiCl_3.AlCl_3$)

(1) *A. Ferna´ndez, E. Deprez , O. Friedrichs. International Journal of Hydrogen Energy 36 (2011) 3931-3940*

EXPERIMENTS

Equipment: Spex 8000 mixer mill

Milling Conditions: ball to power ratio: 20÷1, milling time: 400 min, ball type: stainless steel, 3mm Diameter.

Steel vial and balls

Spex mixer mill

Characterization techniques:

❖ **XRD (X-Ray Diffraction)** using a Bruker D8 Discover
… for phase-identification and assessment of crystallinity of active metals.

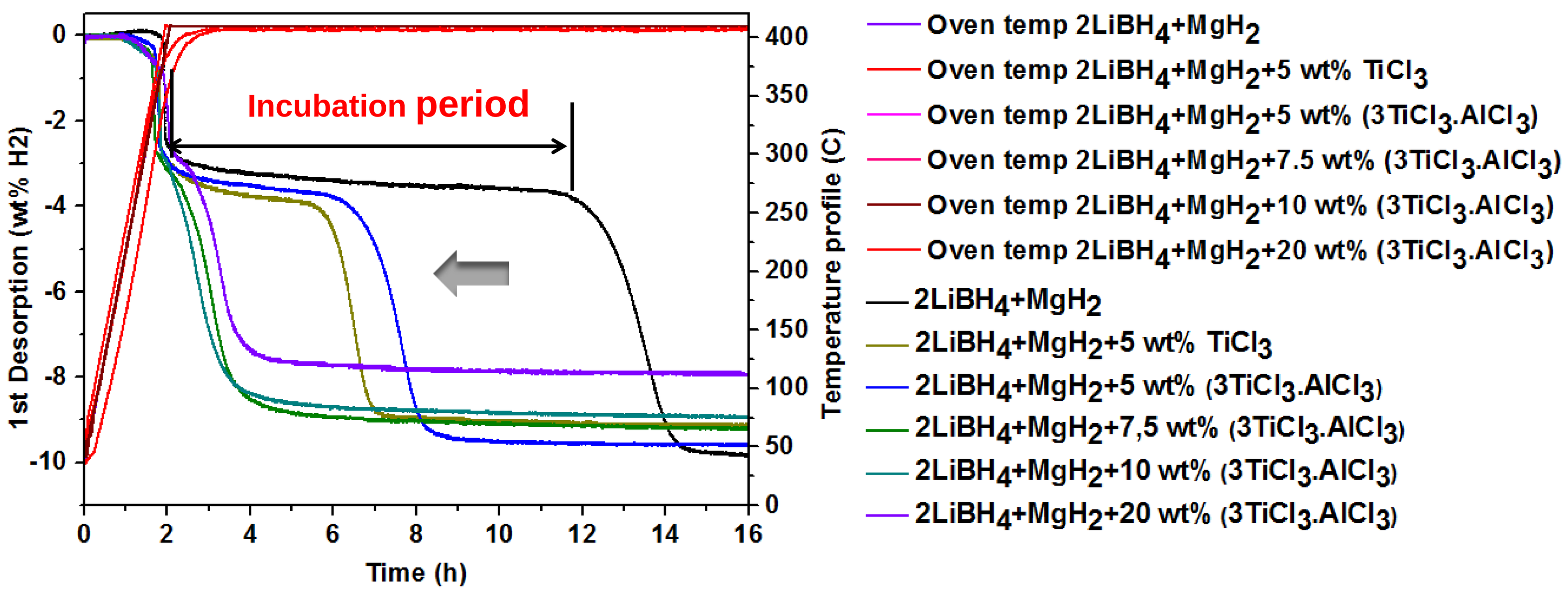
❖ **DTA-TG (Differential thermal-Thermogravimetric** Analysis) using a Netzsch STA 409 C
*… to analyze the change in a property related to an imposed change in the temperature (**thermal analysis**), and the change in the mass of a sample on heating (**thermogravimetric analysis**).*

❖ **In-situ SR-PXD (In-situ Synchrotron Radiation – Powder X-Ray Diffraction)** at the MAX II Lund, Sweden, at Beamline I711
… for non-destructive in-situ analysis of the structure of the material.

❖ **Sievert apparatus:** using a thermo-volumetric Sieverts apparatus designed by Hydro Quebec/ HERA Hydrogen Storage System.
… to perform hydrogen cycling and test the sorption at different stages.

RESULTS AND DISCUSSION

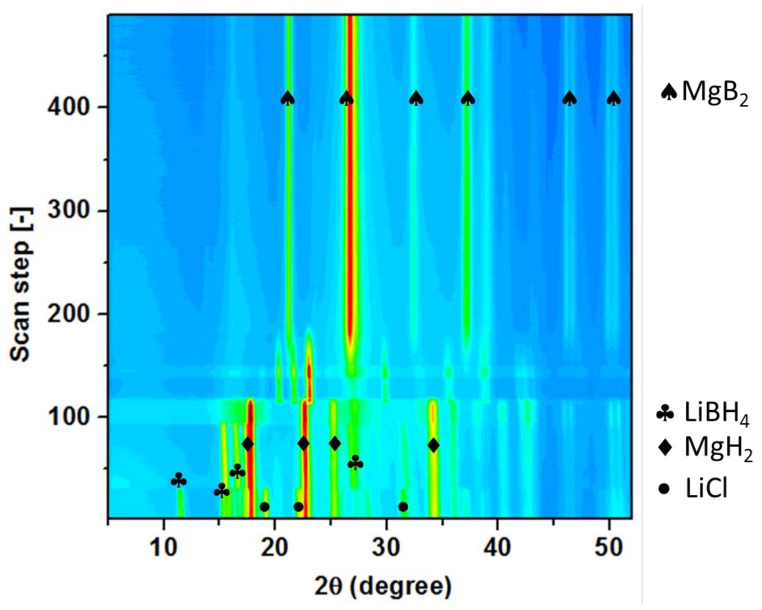
1st Desorption Reaction Kinetics

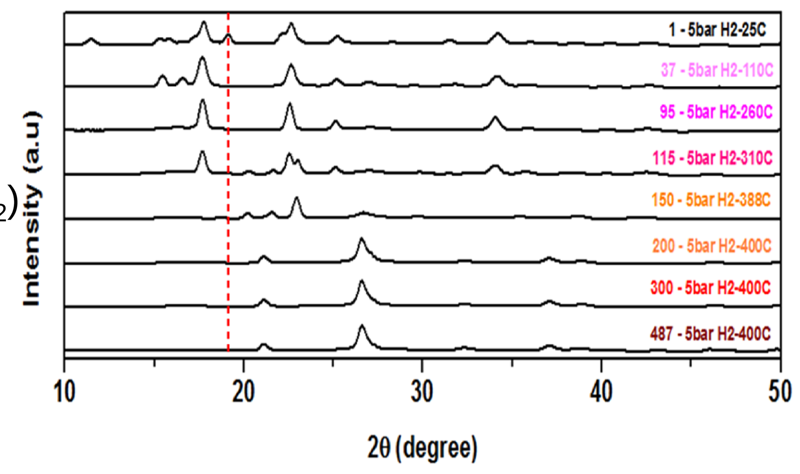


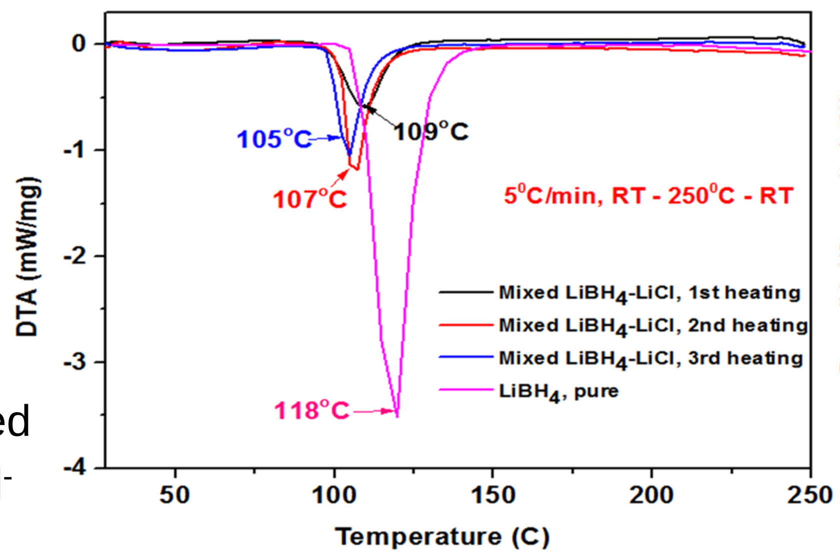
➢ Shorter incubation period for $TiCl_3$/or $3TiCl_3.AlCl_3$ catalyzed 2LiBH4+MgH2 composites.

Solid solution $LiBH_4$ - LiCl

$2LiBH_4$+MgH_2+10wt% ($3TiCl_3.AlCl_3$)
(Desorption: RT to 400^{o}C (5^{o}C/min); 5 bar H_2)



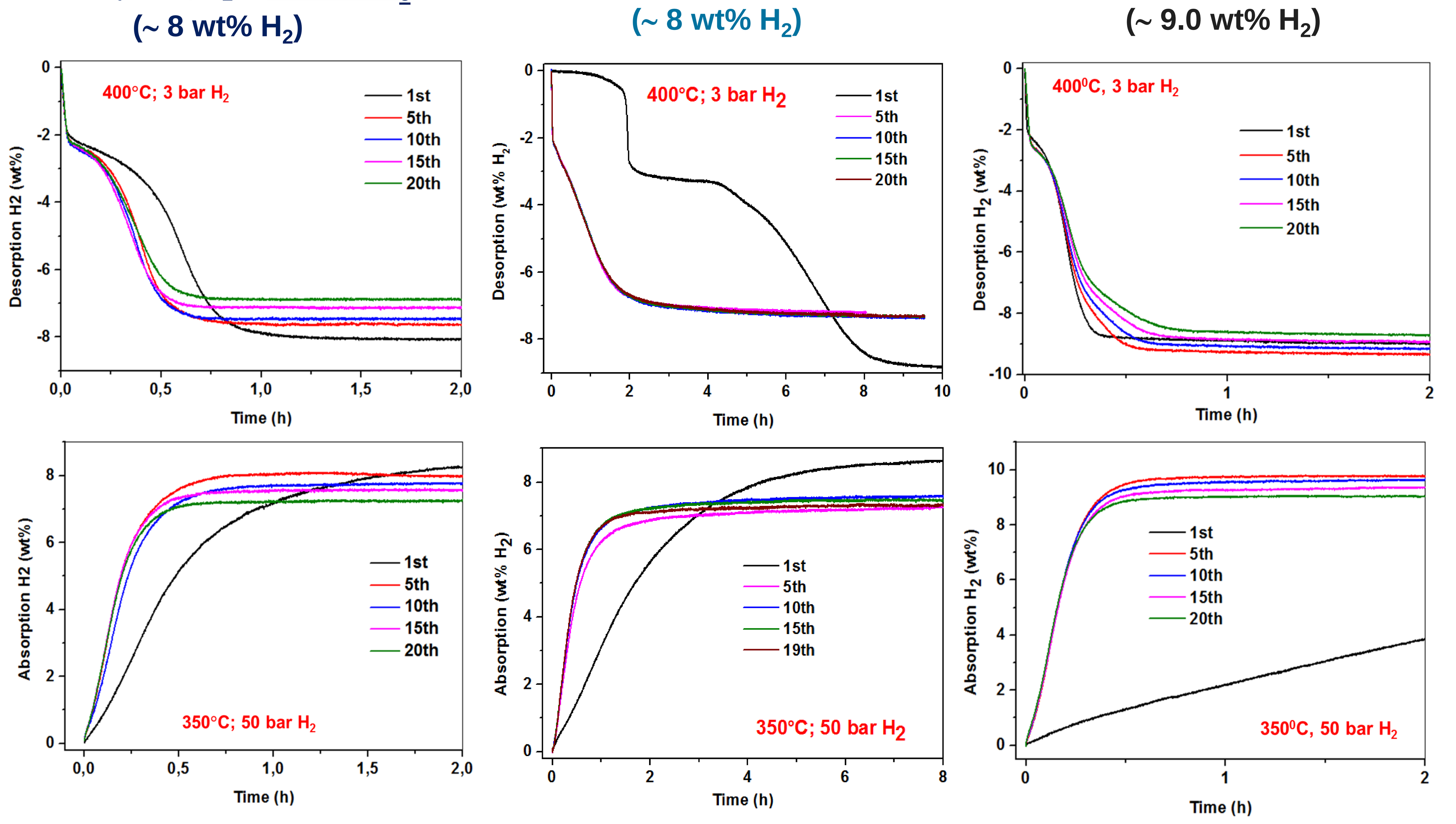




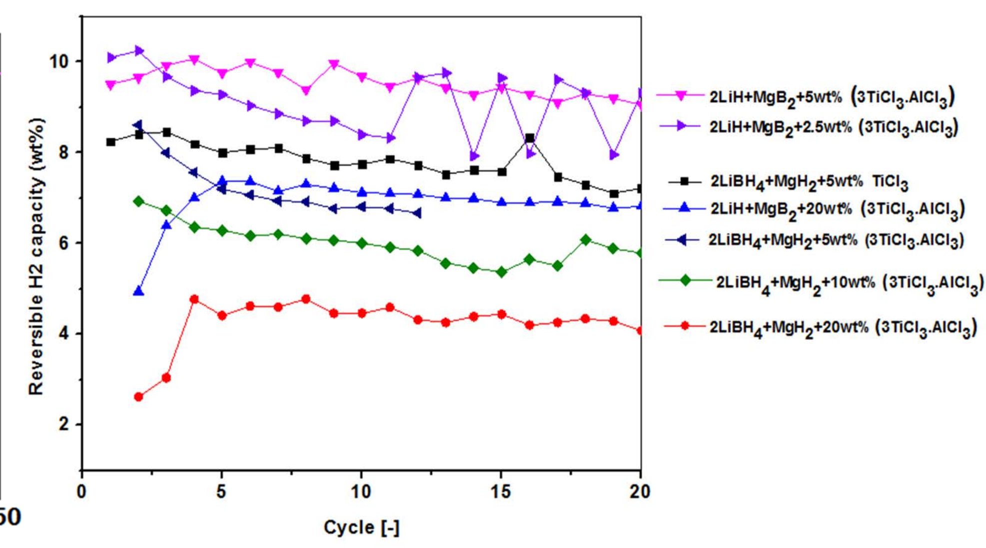
➢ $LiBH_4$ – LiCl solid solution was formed during reaction and substitution of Cl^- may faciliate the rehydrogenation.

Cycling Capability

$2LiBH_4$ + MgH_2 + 5wt%$TiCl_3$ (~ 8 wt% H_2) | **$2LiBH_4$ + MgH_2 + 5wt%($3TiCl_3.AlCl_3$) (~ 8 wt% H_2)** | **2LiH + MgB_2 + 5wt%($3TiCl_3.AlCl_3$) (~ 9.0 wt% H_2)**



Reversible Hydrogen Capacity



➢ ***2LiH + MgB_2 + 5wt%($3TiCl_3.AlCl_3$)** shows the highest hydrogen capacity and fast sorption rate.*

➢ *With adding ($3TiCl_3.AlCl_3$) and $TiCl_3$, desorbed state side is better.*

➢ $LiBH_4$ – LiCl *solid solution → further study on the effect of LiCl on* $2LiBH_4$ + MgH_2 hydrogen storage material.

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