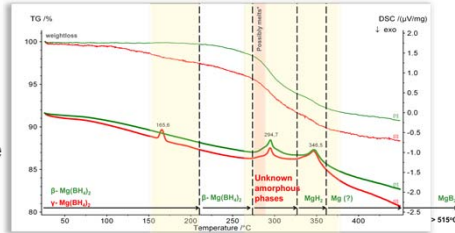


$Mg_2(BH_4)_2$ AS HYDROGEN STORAGE MATERIAL

- Hydrogen storage capacity is amongst the highest of all materials: **15 wt.%** and **55-80 kgH₂/m³**
- Calculations predict **favorable thermodynamics** of H₂ release which means acceptable working temperatures

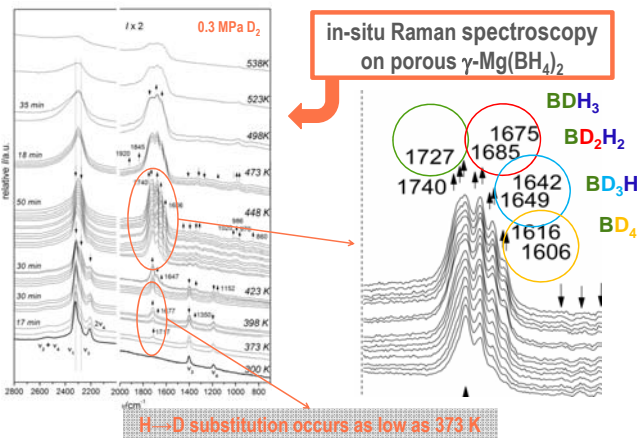
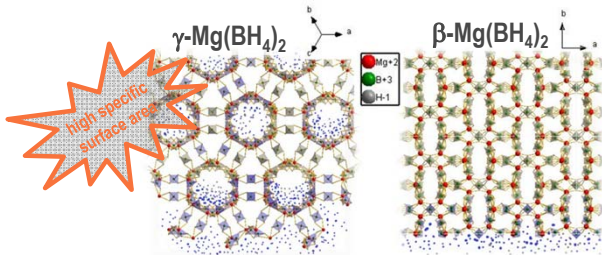
but

- Slow kinetics of desorption
- Harsh conditions for rehydrogenation of the completely decomposed compounds
- Possible release of byproducts such as B₂H₆
- Complicated H₂-release pathway
- Several steps and reaction intermediates unclear



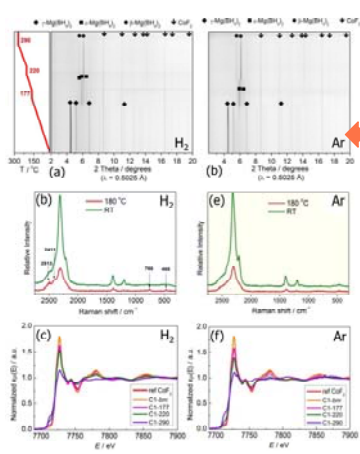
UNDERSTANDING THE RATE-LIMITING REACTION STEPS

Isotopic Exchange in Porous and Dense $Mg_2(BH_4)_2$



in-situ Raman spectroscopy on porous γ - $Mg(BH_4)_2$

simultaneous in-situ X-ray Powder Diffraction, Raman, and X-ray Absorption Spectroscopy

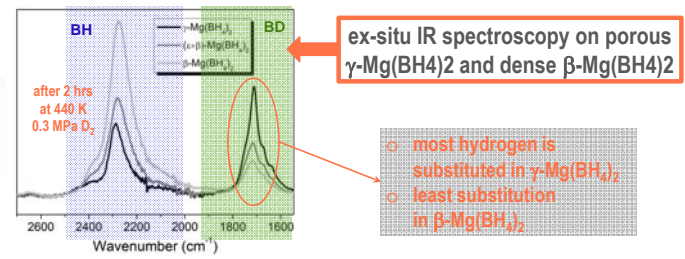
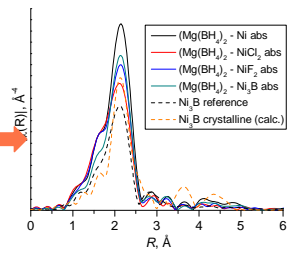


O. Zavorotynska, S. Deledda, J.G. Vitillo, M. Baricco, B.C. Hauback et al., *Energies* 2015, 8, 9173-9190

- The reversible phase is amorphous and is yet to be fully identify
- After cycling, all Ni and Co species show a local structure similar to that of boride-like compounds

X-ray Absorption Spectroscopy for Ni-based additives

I. Saldan, O. Zavorotynska, S. Deledda, B.C. Hauback et al., *J. Phys. Chem. C* 2014, 118, 23376-23384



ex-situ IR spectroscopy on porous γ - $Mg(BH_4)_2$ and dense β - $Mg(BH_4)_2$

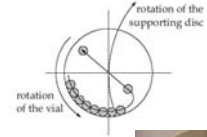
- most hydrogen is substituted in γ - $Mg(BH_4)_2$
- least substitution in β - $Mg(BH_4)_2$

bulk D diffusion is the rate-limiting step in the isotope exchange reactions, and likely in H-sorption reactions in $Mg(BH_4)_2$

O. Zavorotynska, S. Deledda, G. Li, M. Matsuo, S.-I. Orimo and B. C. Hauback, *Angewandte Chemie* 2015, 127, 10738-10741.

REVERSIBILITY, KINETICS, EFFECT OF Ni- AND Co-BASED ADDITIVES

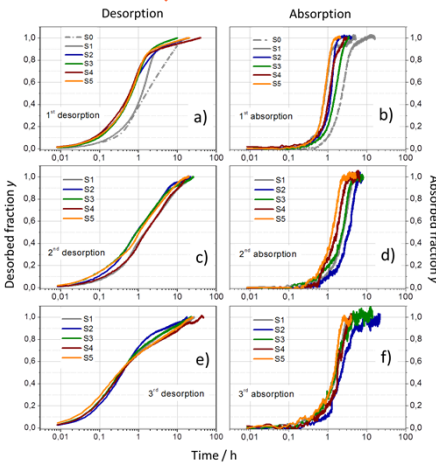
Can ball milling with TM-based additives improve the hydrogen storage properties of $Mg_2(BH_4)_2$



additives tested	
Co ₂ B	Ni ₃ B
CoCl ₂	NiCl ₂
CoF ₂	NiF ₂
CoF ₃	Ni _{nano}
Co ₃ O ₄	



isothermal (500-550 K) hydrogen desorption (2-3 bar H₂) and absorption (120 bar H₂)



O. Zavorotynska, S. Deledda, B.C. Hauback et al., *J. Mater. Chem A* 2015, 3, 6592-6602

- Reversibility can be achieved at desorption and absorption T below 550 K
- Ball milling is enough to speed up the sorption kinetics
- Ni-based and Co-based additives react upon des/abs cycles and do not improve the kinetics significantly

ACKNOWLEDGEMENT

