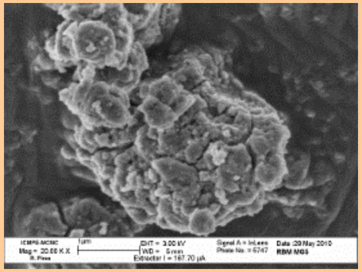
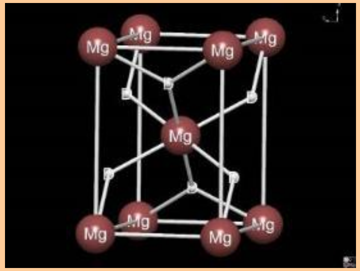
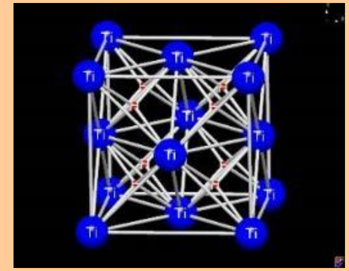
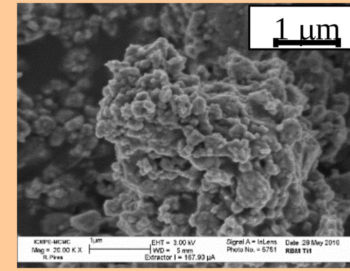




Hybrid Energy Storage Devices and Systems for Mobile and Stationary Applications

Nanostructured materials for solid-state hydrogen storage





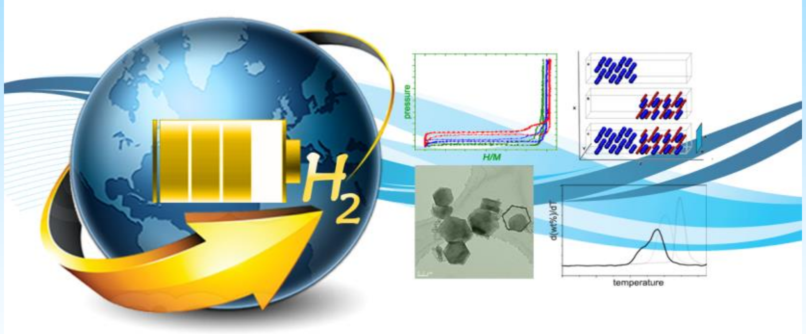
Nanocrystalline Mg-based hydrides for energy storage

Fermín Cuevas* and Michel Latroche

ICMPE/CNRS, Thiais, France

*cuevas@icmpe.cnrs.fr www.icmpe.cnrs.fr

Nanostructured materials for solid state hydrogen storage



COST Action MP1103

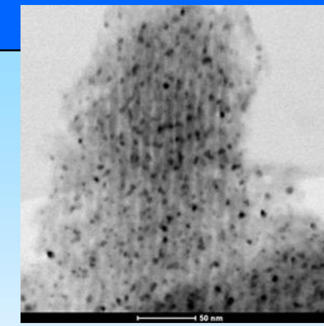
Action Chair: Amelia Montone (ENEA, Italy)

Research aim:

Develop innovative nanostructured materials that meet the targets for practical Solid State Hydrogen Storage (SSHS) for their adequate implementation in stationary and mobile energy storage applications

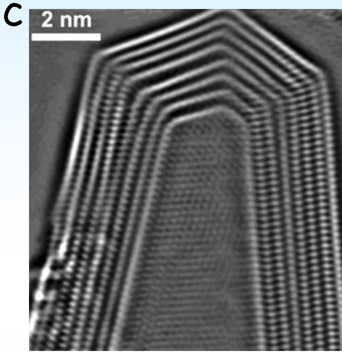
Participants: 26 Countries, ~ 250 members

Organisation: four working groups



- WG1: Synthesis of novel materials with optimized properties

  Group Leader: Fermín Cuevas (CNRS, France)



- WG2: High resolution and high sensitivity characterization of atomic level structure and of microstructural features

  Group Leader: Sara Blas (Belgium)

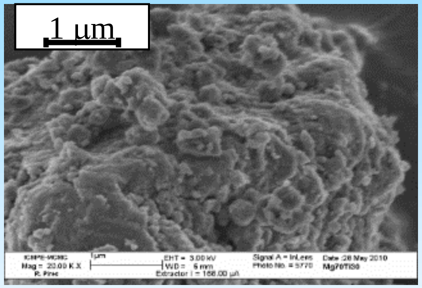
- WG3: Characterization of hydrogen storage properties both at the laboratory level and at the scale of prototype tanks

  Group Leader: Martin Dornheim (HZG, Germany)

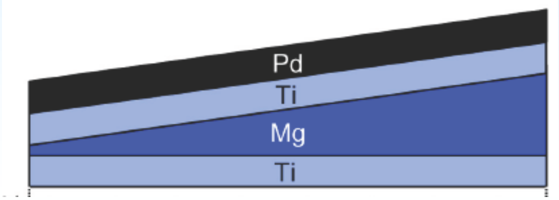
- WG4: Computational modeling of processes relevant to SSHS

  Group Leader: Tejs Vegge (Denmark)

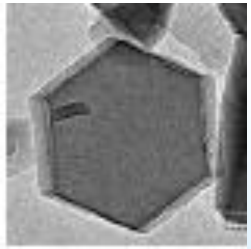
Management of Synthesis WG: architecture - based



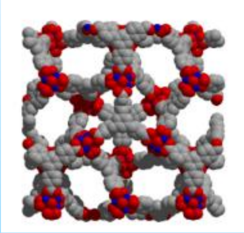
Task 1: Nanostructured bulk materials.
Leader: Torben Jensen
(Aarhus University, Denmark)



Task 2: Thin films.
Leader: Bernard Dam
(Delft University of Technology, Netherlands)



Task 3: Nanoparticles and core-shell structures.
Leader: Kondo-Francois Aguey-Zinsou
(University of New South Wales, Australia)



Task 4: Porous and nanoscaffold hybrid materials.
Leader: Michael Hirscher
(Max Planck Institute for Intelligent Systems, Germany)

Outline

- Introduction: Mg for solid-state hydrogen storage
- Synthesis: Reactive ball milling under hydrogen
- Applications:
  - MgH_2-TiH_2 for solid-state hydrogen storage
  - Mg_2TMH_x (TM = Fe, Co, Ni) for Li-ion batteries
- Conclusions

Universal material requirements for energy storage

- Reversibility under operating conditions
- High specific and volumetric energy densities
- Fast loading and unloading kinetics
- Long cycle life
- Environmentally friendly
- Safety
- Low-cost

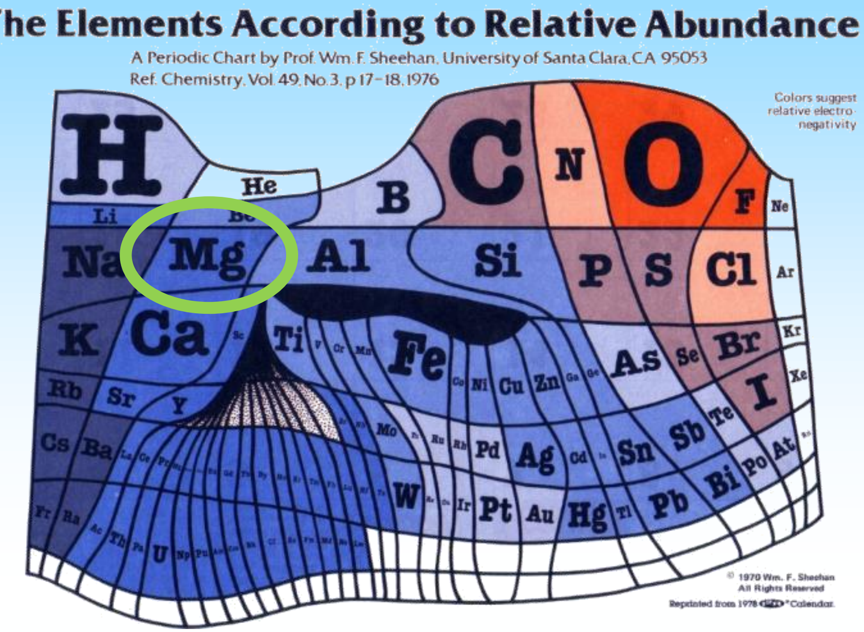
Magnesium for solid-state hydrogen storage

Advantages

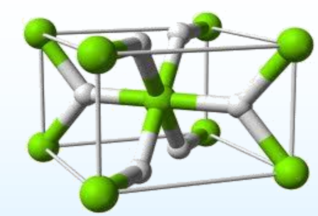
Abundant, low-cost, light-weight

Simple hydrogen reaction

$$Mg_{(s)} + H_{2(g)} \leftrightarrow MgH_{2(s)}$$



High storage capacity : **7.6 wt.% H, 109 gH_2/L**



Drawbacks

Too stable hydride for RT applications : P_{eq,H_2} = 1 atm at 280 °C

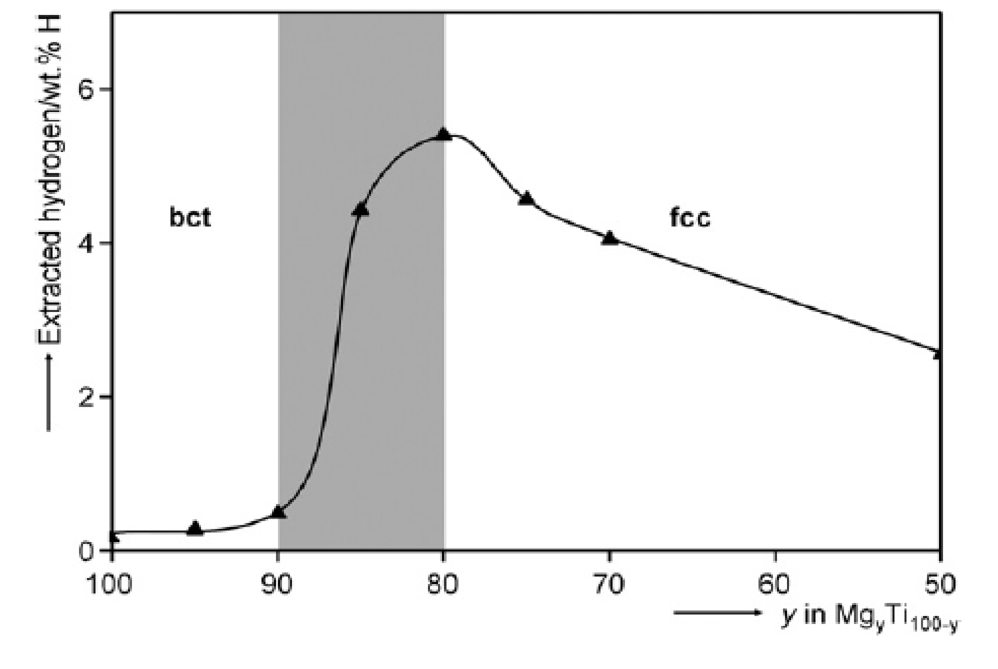
Slow sorption kinetics

Applications: Ni-MH electrochemical storage

- Negative electrode of Ni-MH battery $Mg + xH_2O + xe^- \rightleftarrows MgH_x + xOH^-$

✓ Kinetics enhancement: Ti-incorporation in Mg lattice

transition from bct-rutile (MgH_2) to fcc-fluorite (TiH_2) structure



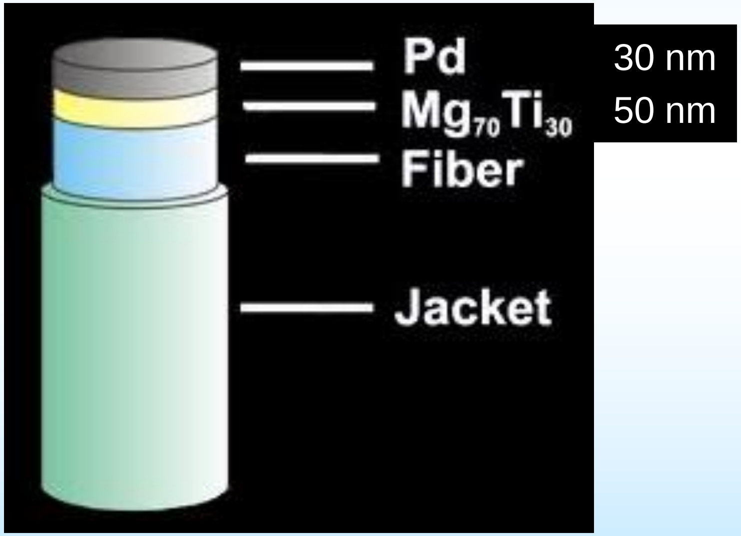
Vermeulen et al., J. Mater. Chem., 2008, 18, 3680

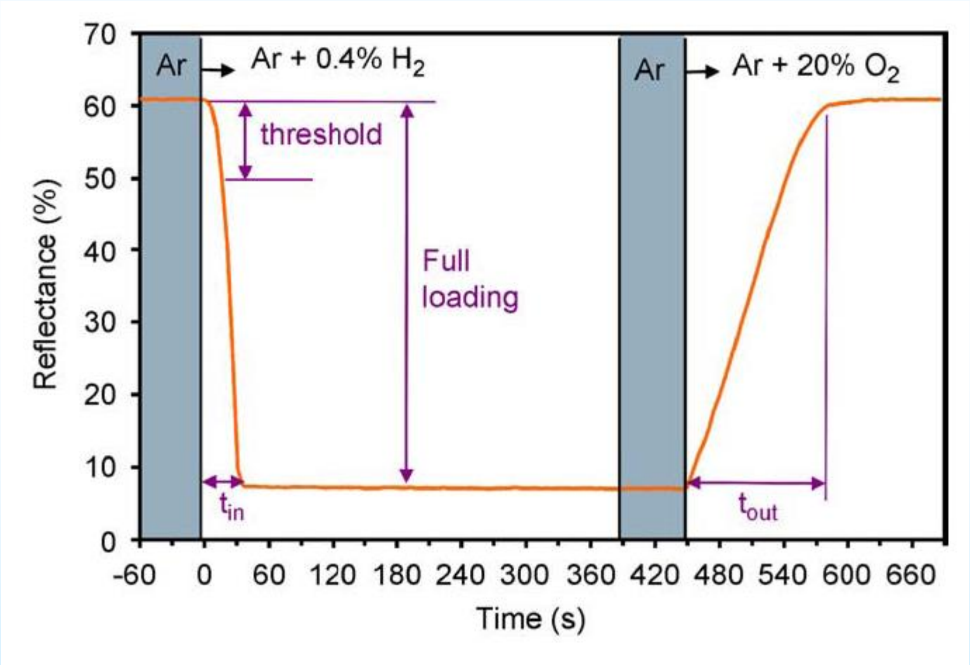
Applications: hydrogen sensors

- Solid-gaz hydrogen absorption induces a metal to semiconductor transition

$$\mathbf{Mg\ (metallic) + H_2 \rightleftarrows MgH_2\ (semiconductor)}$$

✓ Kinetics enhancement: thin film technology, Ti-incorporation, Pd coverage





Slaman et al., Sens. Actuators B, 2007, 123, 538

Applications: hydrogen storage for grid regulation

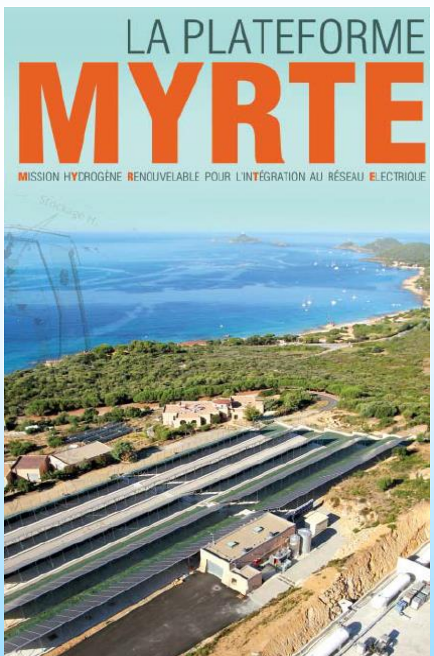
- Principle: regulation of electricity generation from intermittent sources

Electrolytic H_2 production → H_2 Storage → Fuel cell

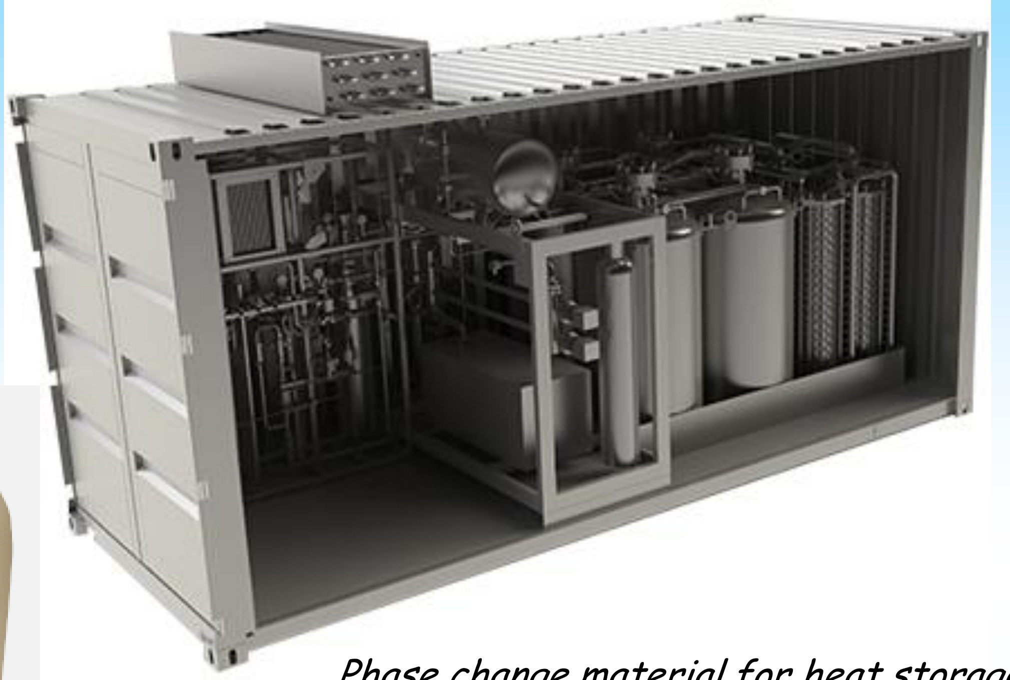
Irregular electricity generation → Excess → Electrolytic H_2 production

Fuel cell $\xrightarrow{\delta t}$ Stabilized electricity supply

Irregular electricity generation → Stabilized electricity supply

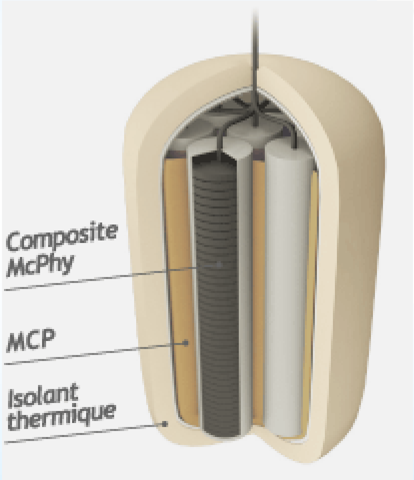


Hydrogen storage: Mg-based nanohydride

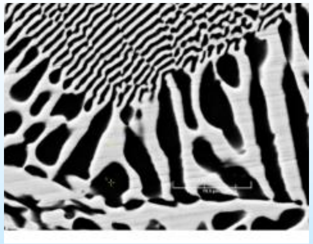


Composite: MgH_2 + graphite

Compressed composite



Phase change material for heat storage
$Mg_{69}Zn_{28}Al_3$



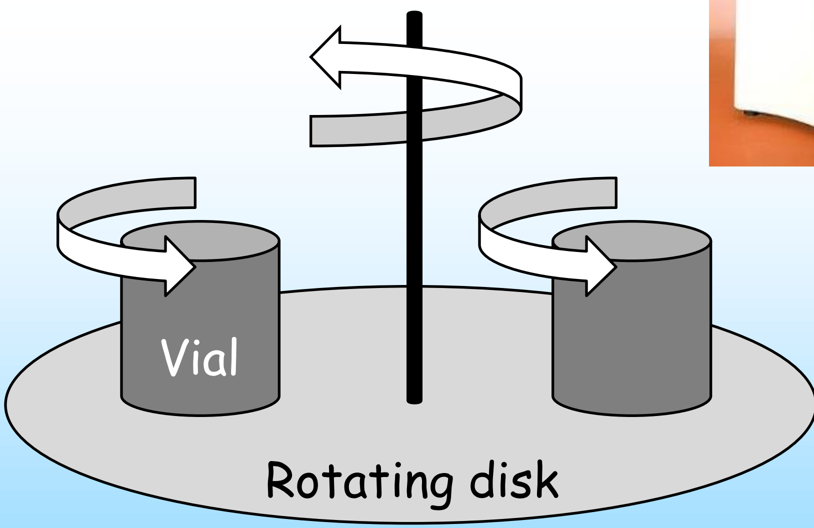
Garrier et al., Int. J. Hydrogen Energy, 2013, 38, 9766

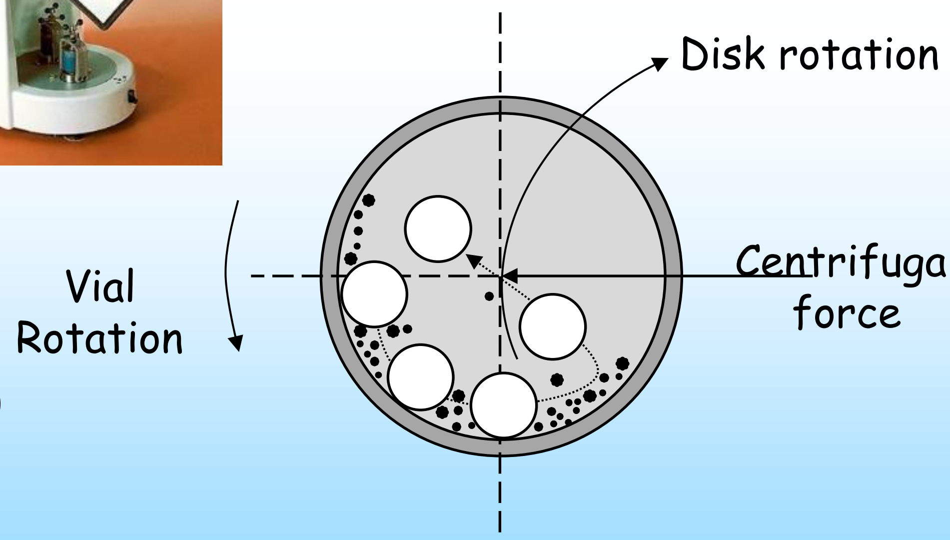
✓ Kinetics enhancement: nanostructuration by milling, additives, temperature

Reactive ball milling (RBM) under hydrogen

Ball milling: the planetary principle

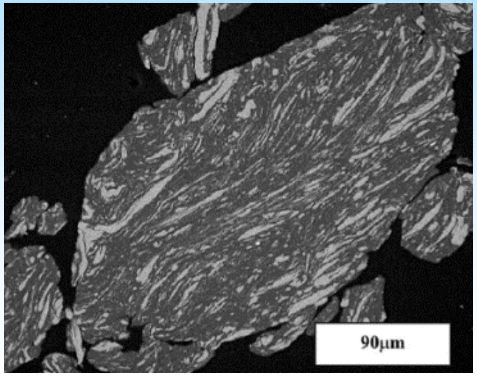
- Eccentrically vials rotating in opposite direction to the supporting disk.
- The planetary movement generates balls take-off.
- Balls collide between them and with vial walls, crashing by friction and impact the powders inside the vial.





Ball milling: nanostructuration

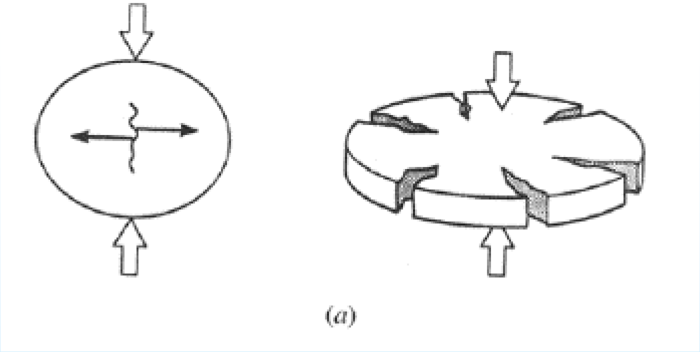
Repeated solid state fragmentation and cold welding



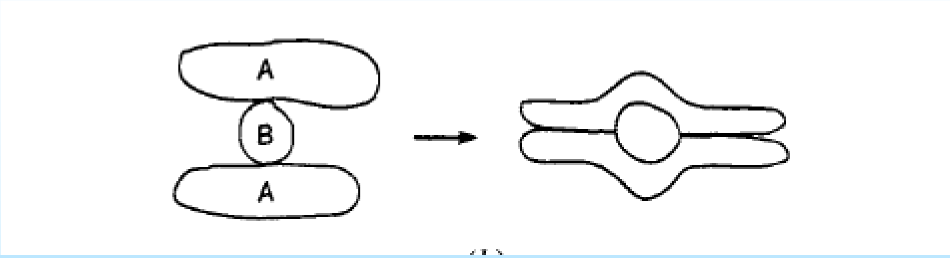
Synthesis of nanocomposites: Ni-superalloys / oxide

1970. *J. Benjamin, Met. Trans. 1 (1970) 2943*

Fracture: fresh surfaces, size-reduction



Welding: solid-state reactions, mixing

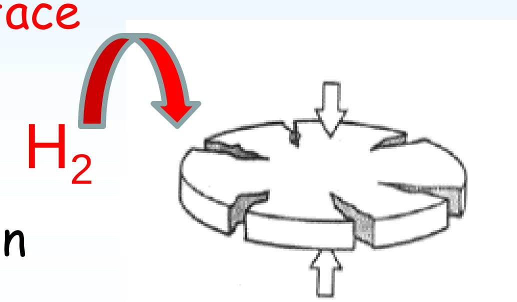


D.R. Maurice and T.H. Courtney: Metall. Trans. A, 1990, vol. 25A, pp. 147-157

RBM under hydrogen: fast synthesis of nanohydrides

Fracture on milling

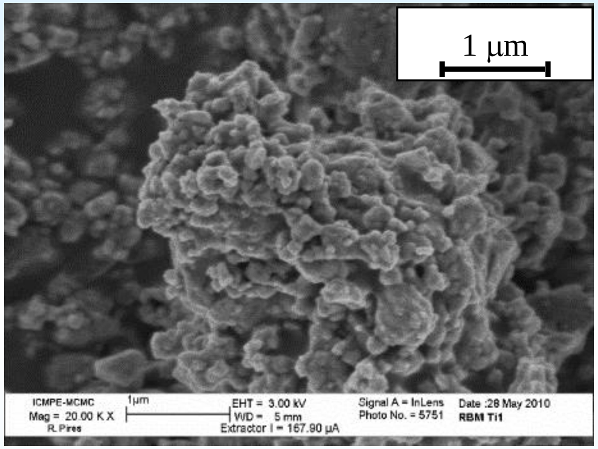
Generation of fresh surfaces
$\Rightarrow$ Clean solid-gas interface



Hydrogen absorption

Hydrogen embrittlement

Particle size refinement



TiH_2 - nanohydride

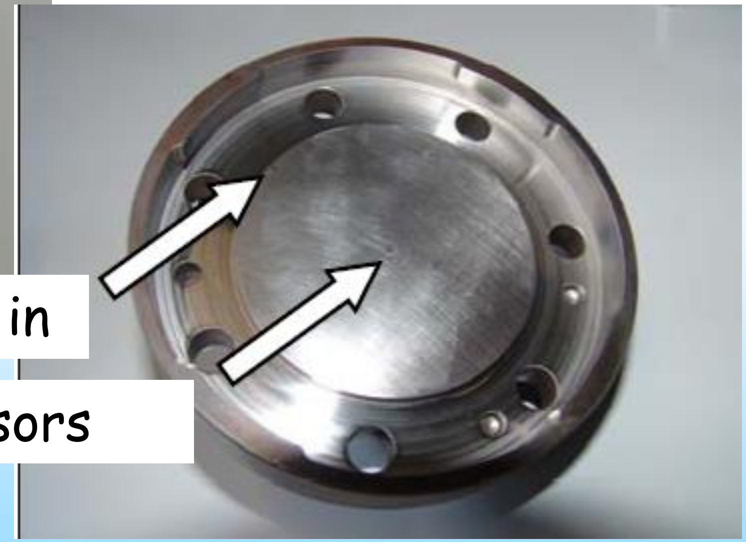
RBM under hydrogen : Evicomagnetics commercial device

H_2

$Pi(H_2)$ = 150 atm

Vial volume: 200 ml

Monitoring of P and T



H_2 in

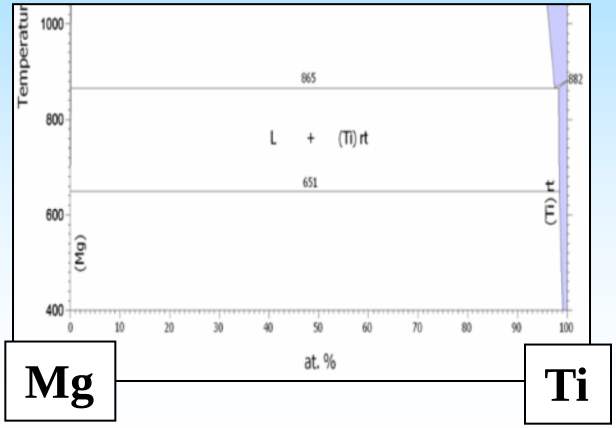
P,T sensors

S. Doppiu et al. J. Alloys Comp. 427 (2007) 204

MgH_2-TiH_2 nanocomposites for solid-state hydrogen storage

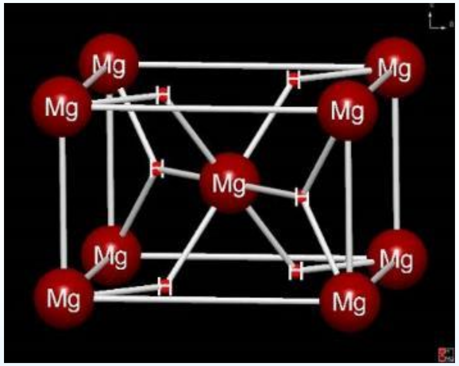
Mg-Ti system and binary metal hydrides

- Mg-Ti: an immiscible system



+ H_2

MgH_2

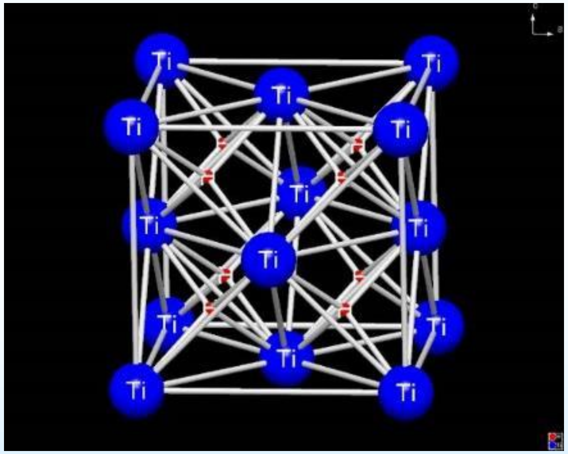


D (300 K) ~ 10^{-12} cm^2 s^{-1}

Rutile-type structure

+ H_2

TiH_2

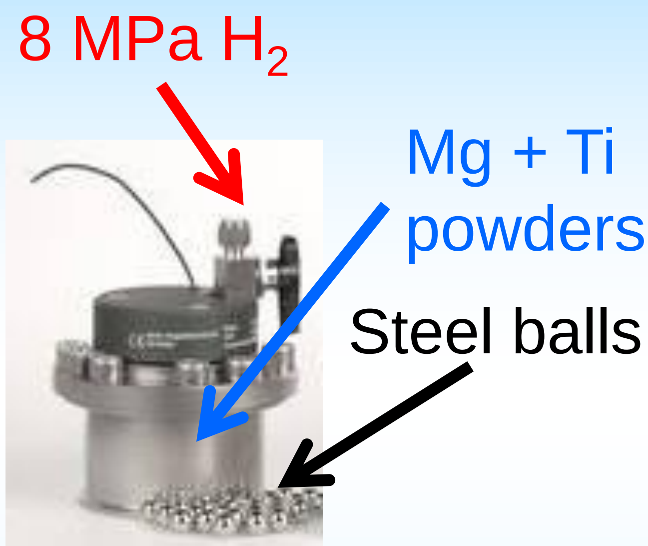


D (300 K) ~ 10^{-7} $cm^2 s^{-1}$

Fluorite-type structure

Synthesis of (1-y)MgH_2-yTiH_2 nanocomposites

- Evicomagnetics commercial vial: In-situ monitoring of P and T



Vial: hardened SS

Vial volume: 200 ml

Milling device: Fritsch P4

Disk speed: 400 rpm

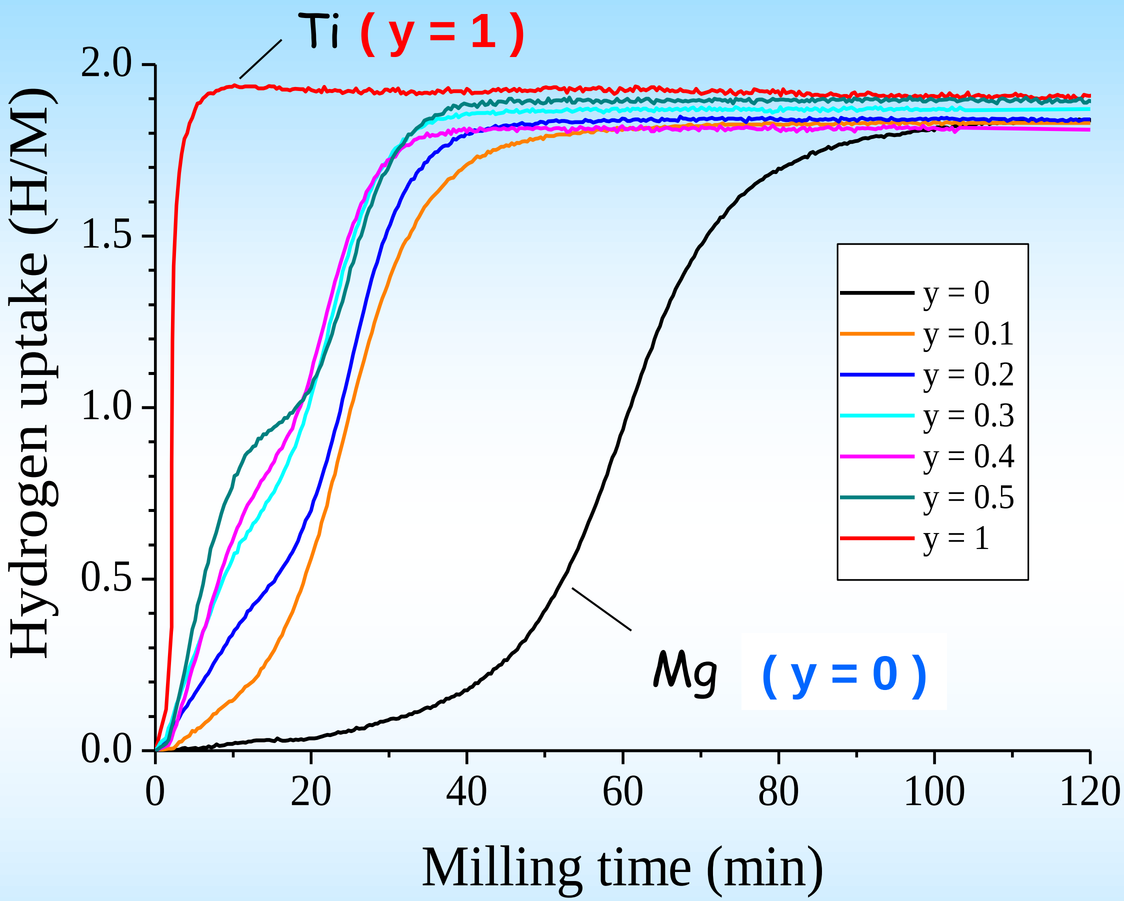
Vial speed: - 800rpm vs. disk

Balls: SS, ∅ = 12 mm

$m_{metal\ powder}$: 5 g

$m_{Balls:\ powder}$ = 60:1

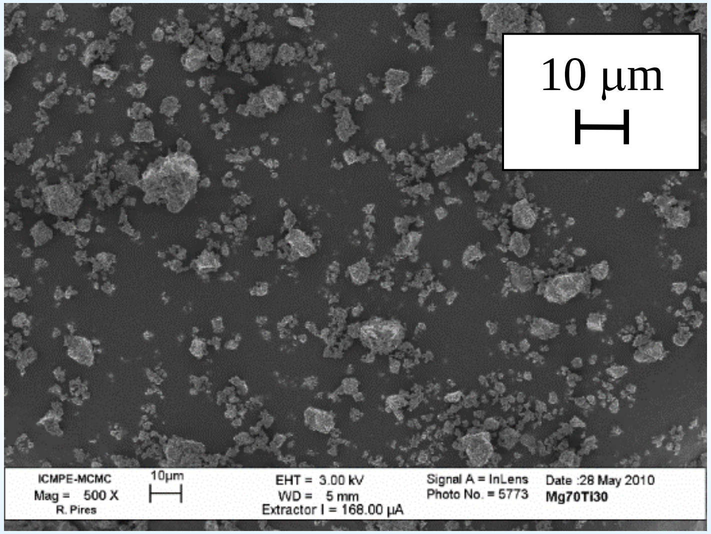
In-situ absorption curves

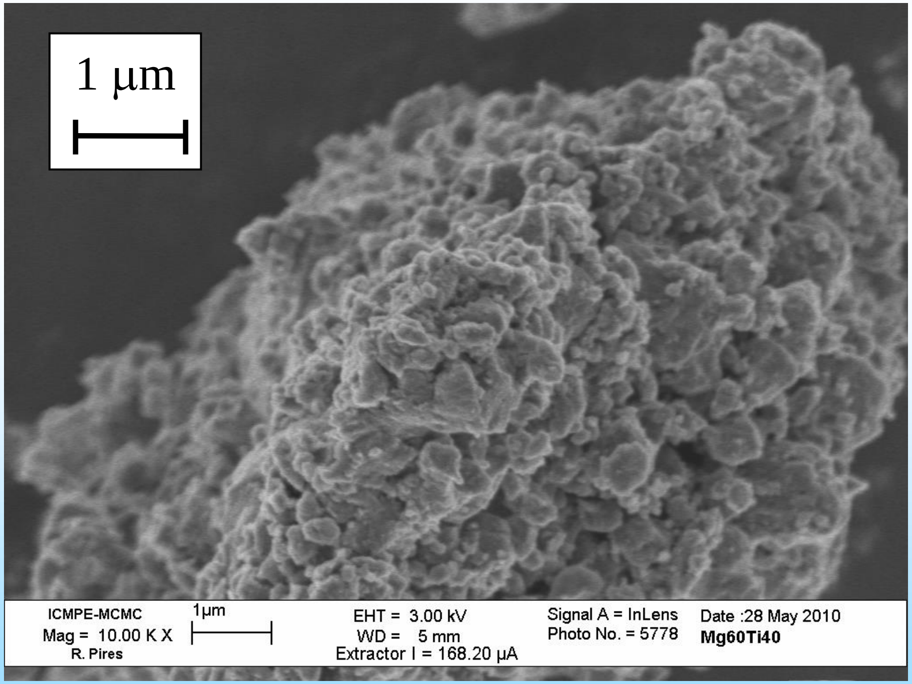


- Fast nanocomposite synthesis (< 1h)
- Two steps: consecutive formation of TiH_2 and MgH_2 phases

MgH_2-TiH_2 powder morphology: SEM analysis

- Reactants: Mg (< 800 µm), Ti (< 150 µm)
- Product: Micrometric-size agglomerates of nanoparticles



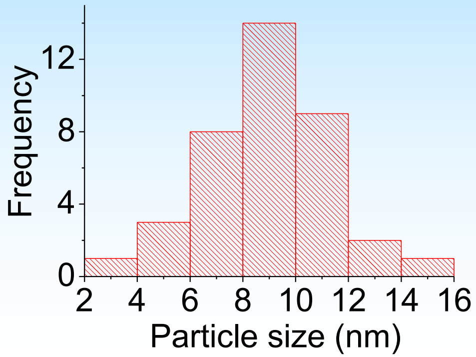


MgH_2-TiH_2 microstructure: TEM analysis

BF-mode

$0.7MgH_2$-$0.3TiH_2$

DF-mode (TiH_2 – selection)



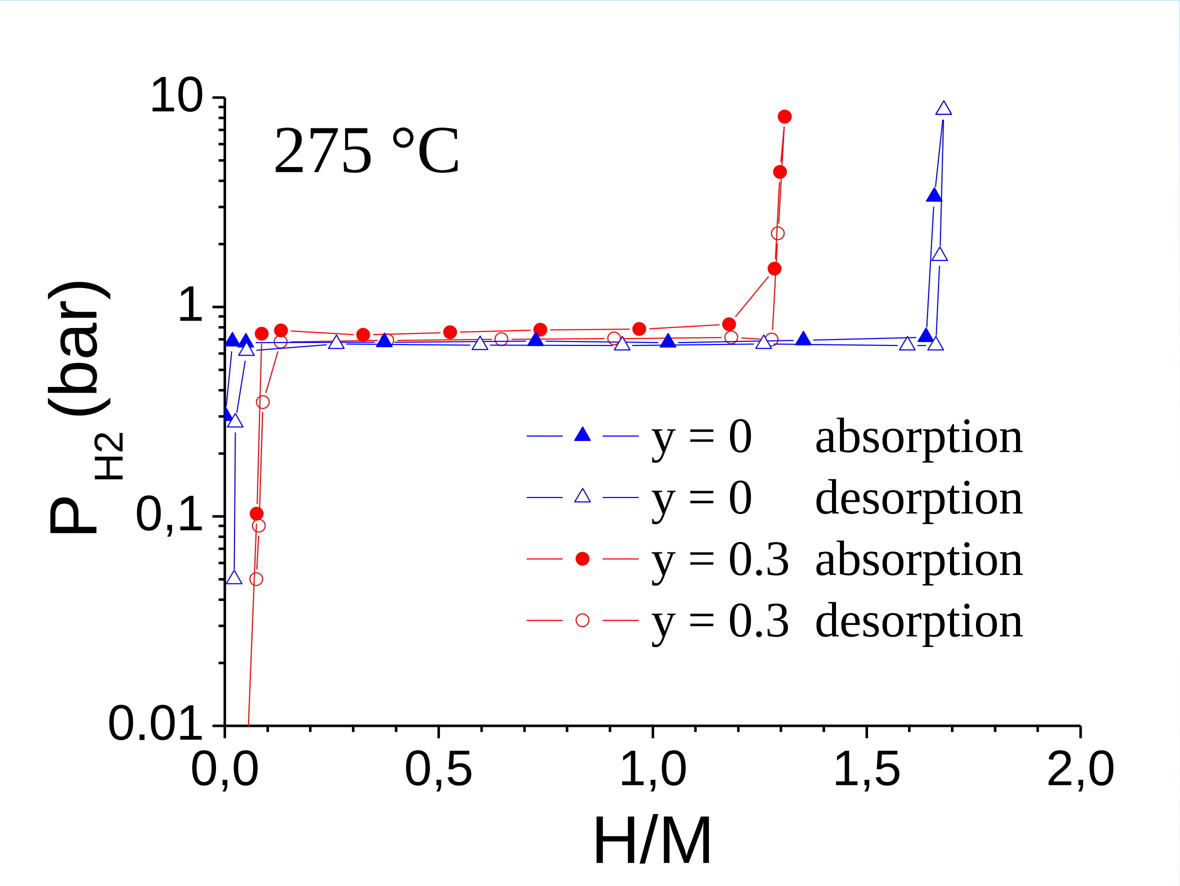
- Homogeneous mixing of MgH_2 and TiH_2 phases at nanoscale
- TiH_2 grain size: ~ 10 nm

Hydrogen storage properties

Comparative study between

MgH_2 (y = 0) and $0.7MgH_2$-$0.3TiH_2$ (y = 0.3)

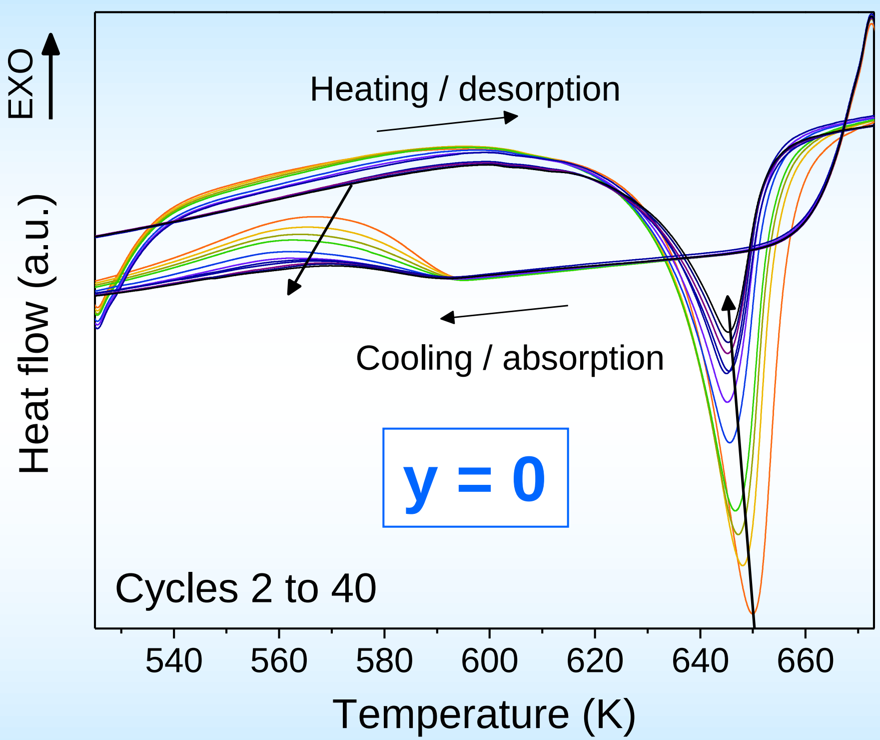
H-thermodynamics



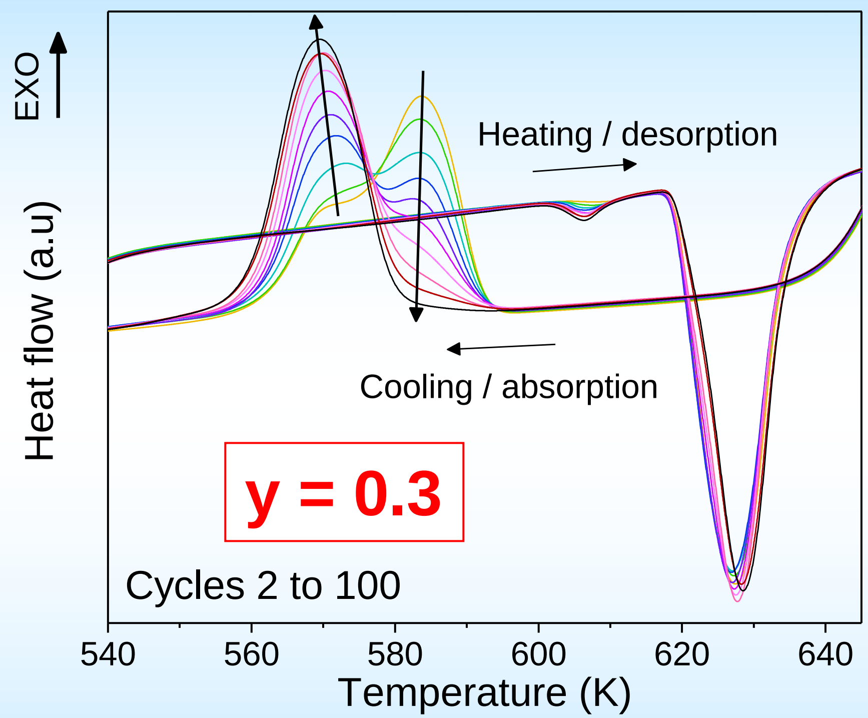
- Only hydrogen from MgH_2 phase is reversibly stored
- No significant changes in Mg-H thermodynamics

Hydrogen cycling at constant pressure (0.4 MPa) : HPDSC

MgH_2

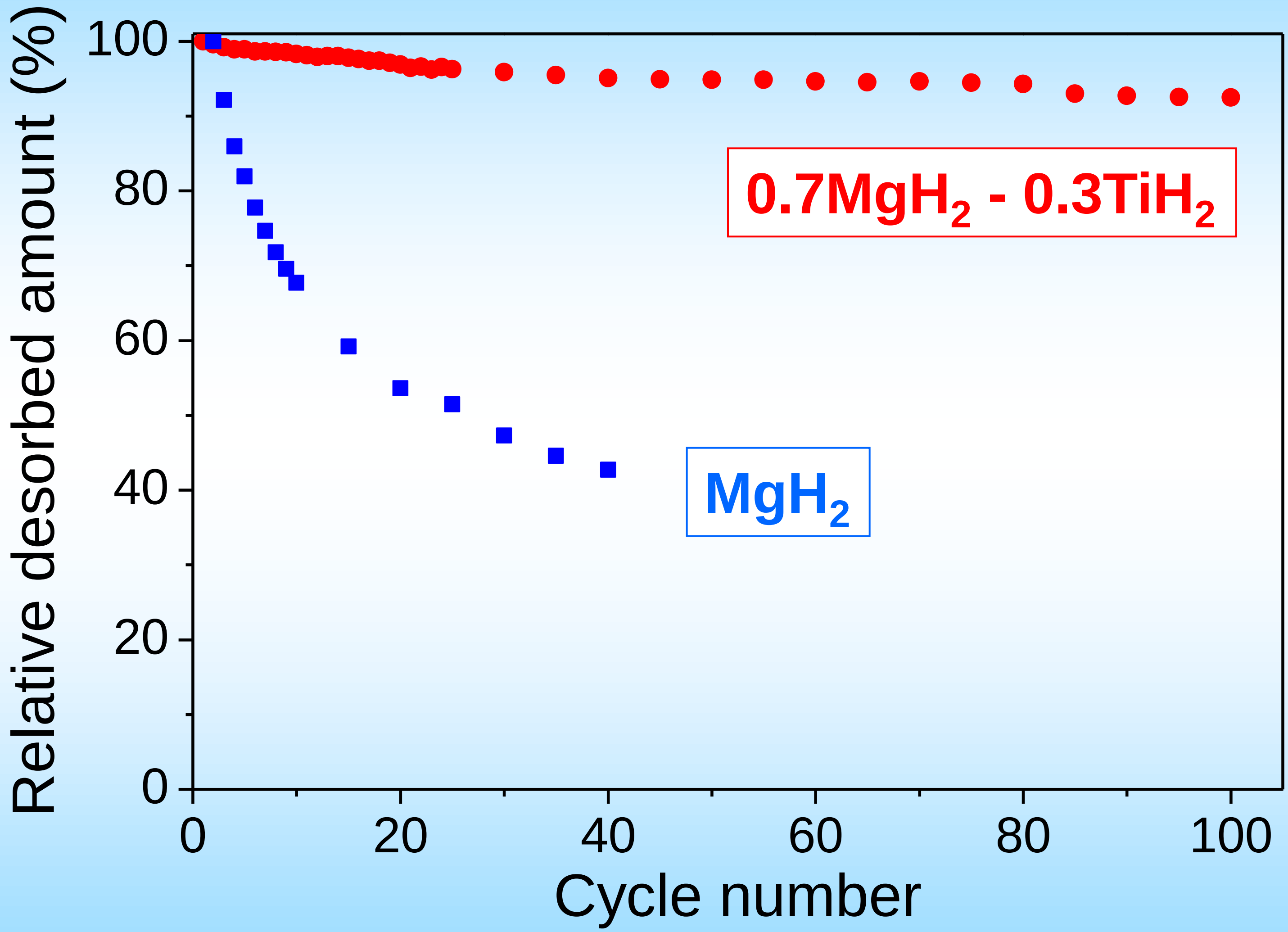


$0.7MgH_2$ - $0.3TiH_2$

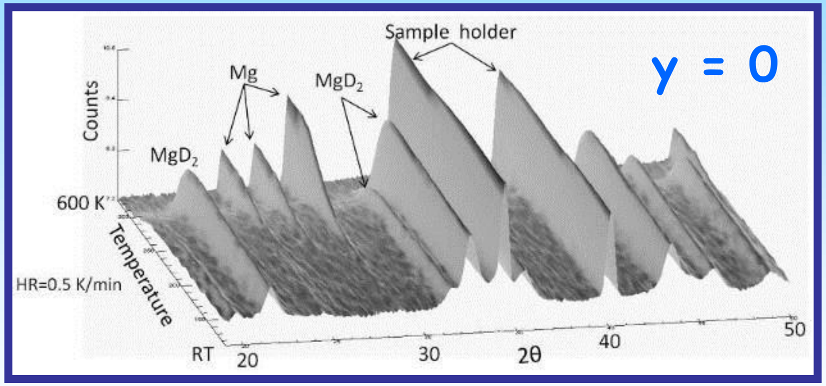


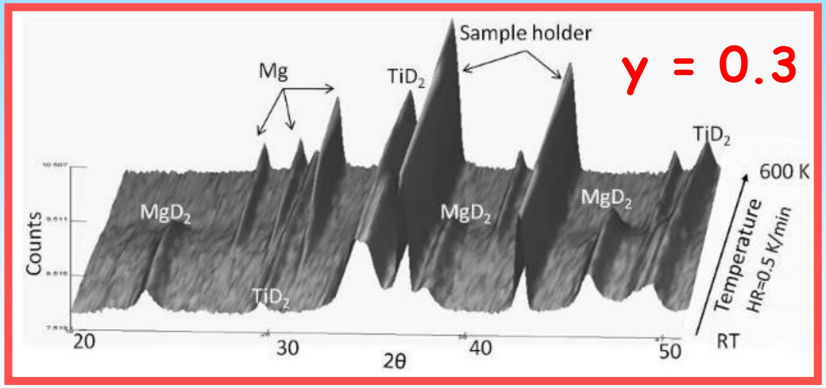
- *Good reversibility for Ti-containing sample*

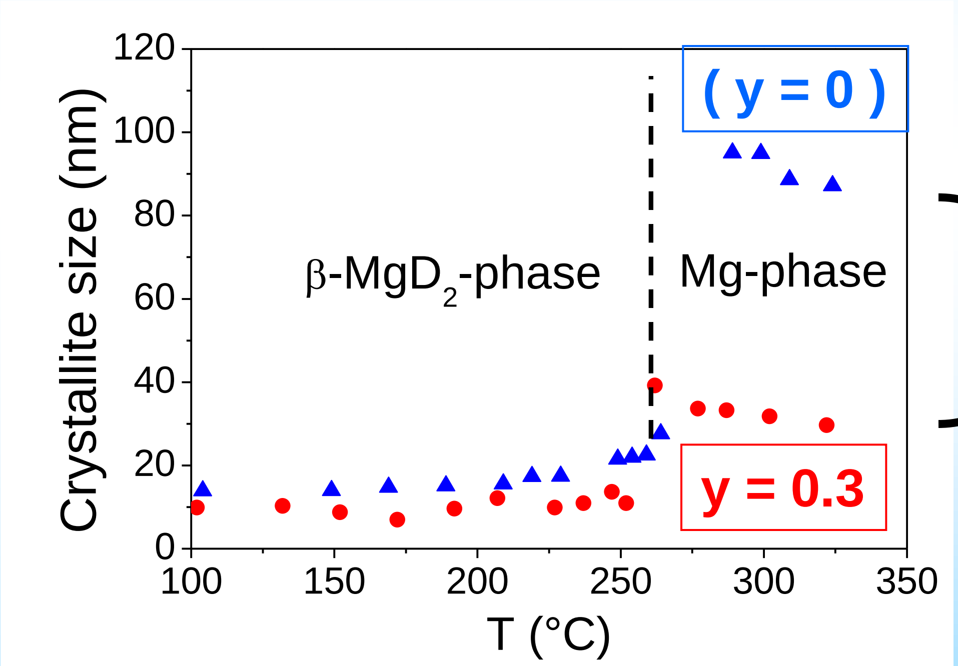
Hydrogen cycling at constant pressure (0.4 MPa) : HPDSC



Hindering of MgH_2 grain coarsening by TiH_2 inclusions

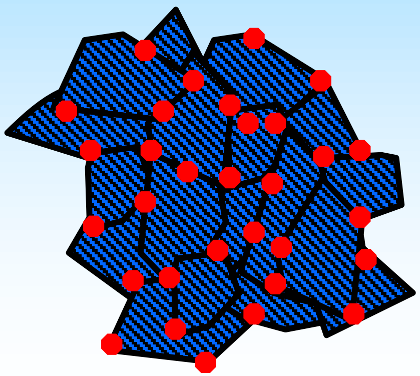


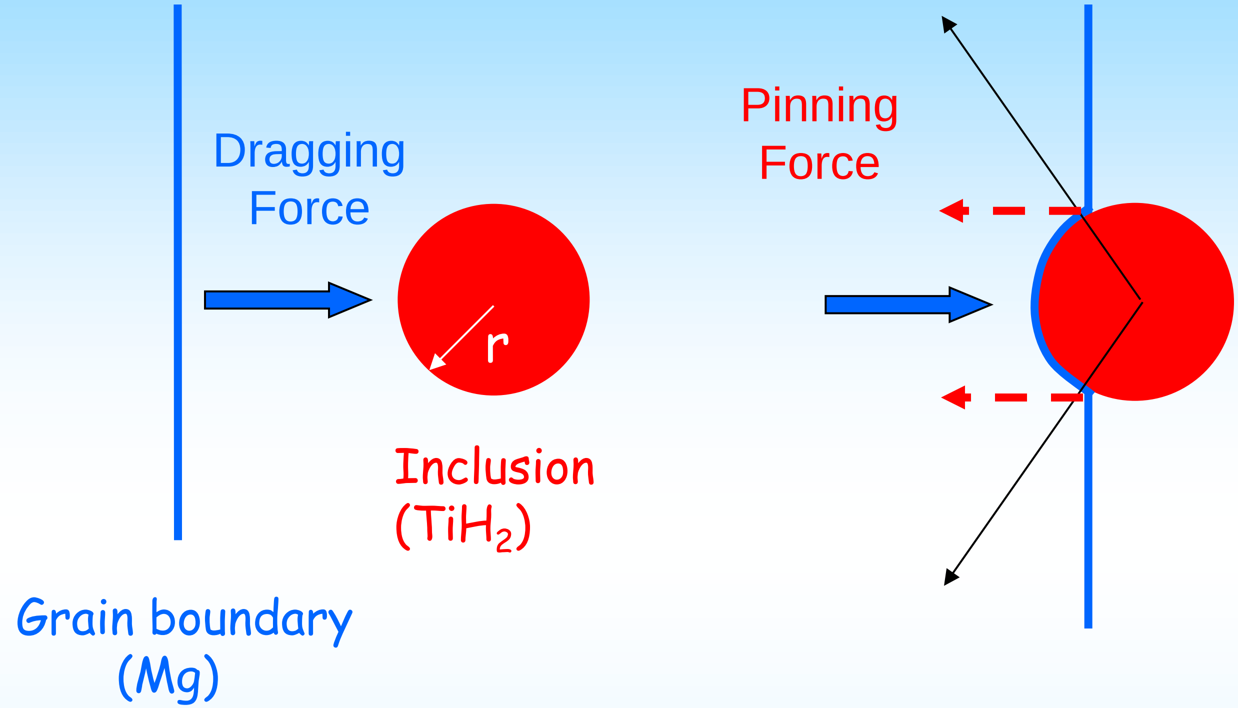




- TiH_2 phase limits grain coarsening of Mg phase

Grain coarsening: Zener pinning effect





- Limited grain growth:

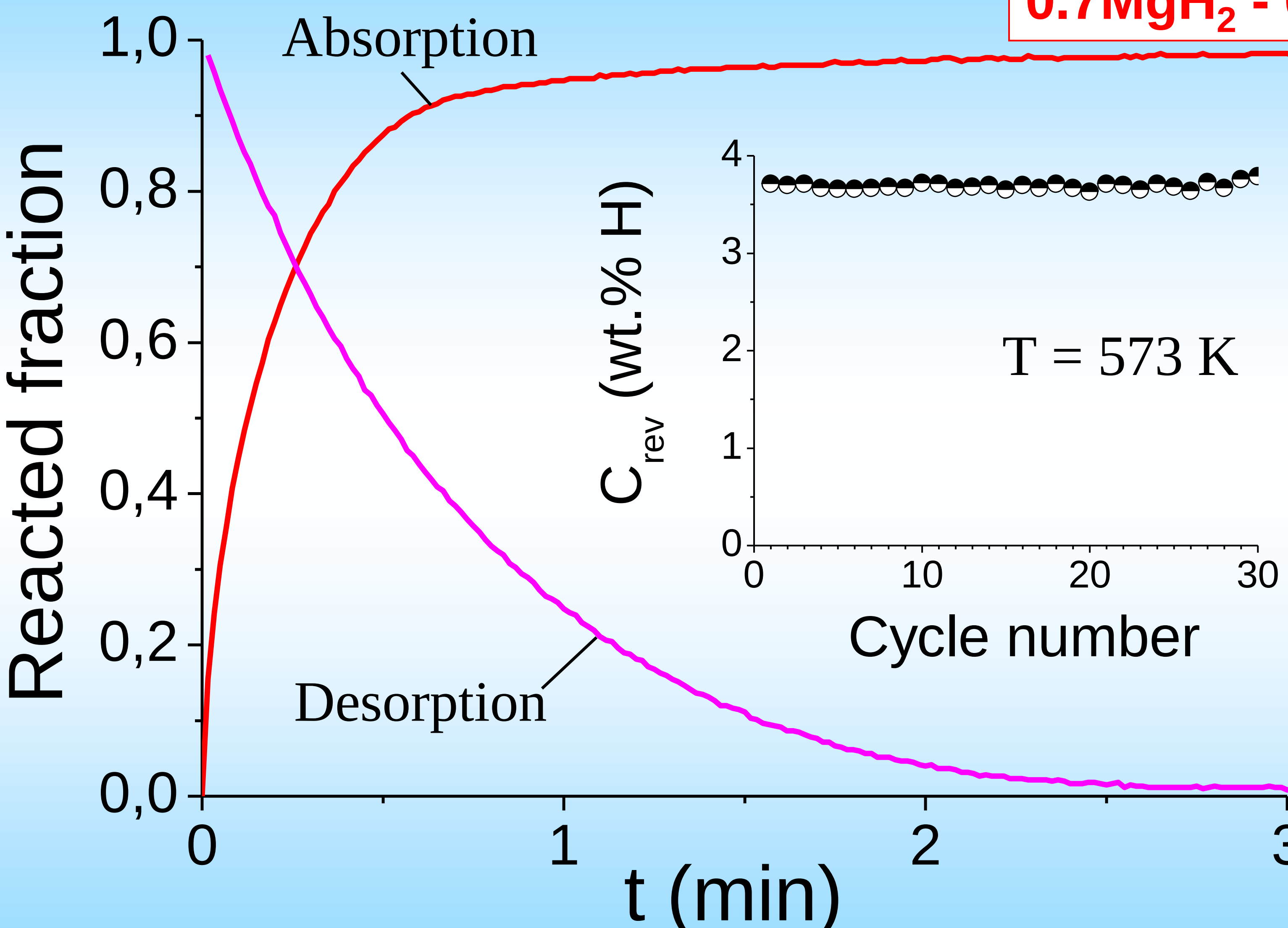
$$< L_c >_{max} = k\,\frac{r}{f}$$

r = radius of inclusions

f = volume fraction of inclusions

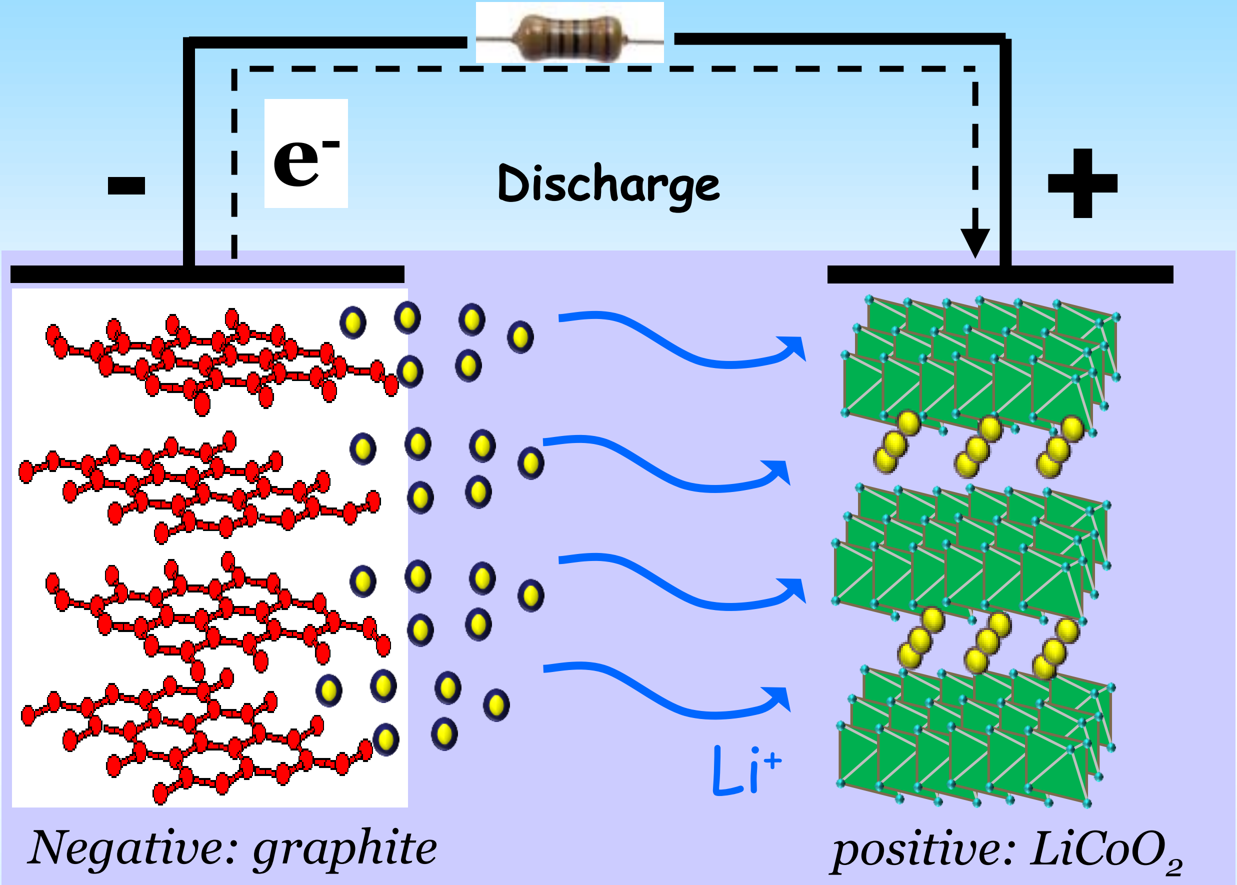
MgH_2-TiH_2 nanocomposites: fast and cycling-stable kinetics

$0.7MgH_2$ - $0.3TiH_2$



Mg_2TMH_x (TM = Fe, Co, Ni) nanohydrides for Li-ion batteries

Classical Li-ion batteries: insertion reactions



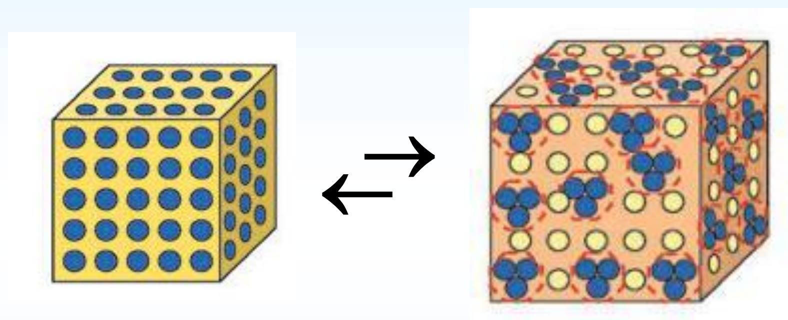
Negative electrode: graphite ($Li_xC_6 \rightarrow 6C + xLi^+ + xe^-$)

Positive electrode: lamellar oxides ($Li_{1-x}MO_2 + xLi^+ + xe^- \rightarrow LiMO_2$)

Graphite substitution by conversion electrodes

$$MA_{x(s)} + x\,Li^{+} + xe^{-} \rightleftarrows M_{(s)} + xLiA_{(s)}$$

A = O, S, N, P, F…



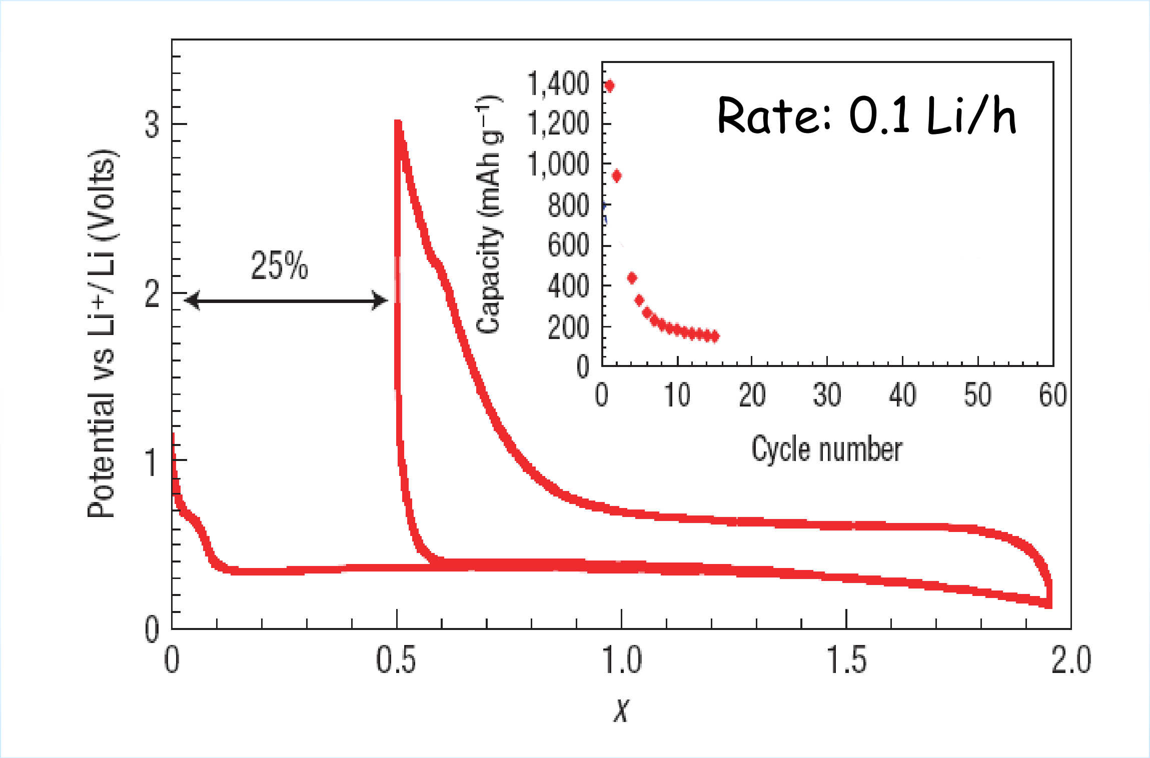
… and hydrides!

$$MH_{x(s)} + x\,Li^{+} + xe^{-} \rightleftarrows M_{(s)} + x\,LiH_{(s)}$$

Oumellal et al. Nature Materials 7 (2008) 916

Ball-milled MgH_2

$$MgH_2\ (s) + 2\ Li^+ + 2e^- \rightleftarrows Mg\ (s) + 2\ LiH\ (s)$$



Capacity: 2038 mAh/g

Reversibility: 75 %

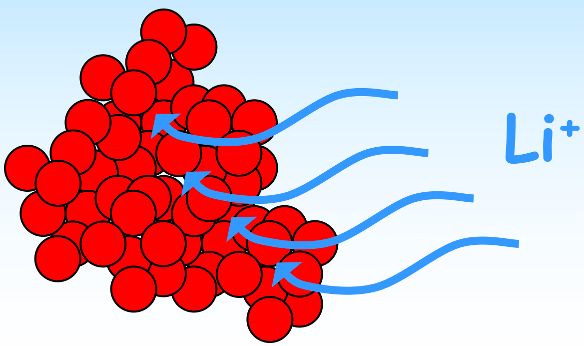
Slow kinetics

Poor cycle life

Oumellal et al. Nature Materials 7 (2008) 916

Challenges

$$MgH_2\,(s) + 2\,Li^+ + 2e^- \rightleftarrows Mg\,(s) + 2\,LiH\,(s)$$



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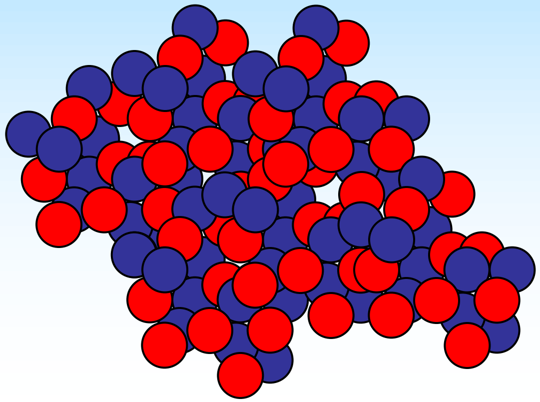


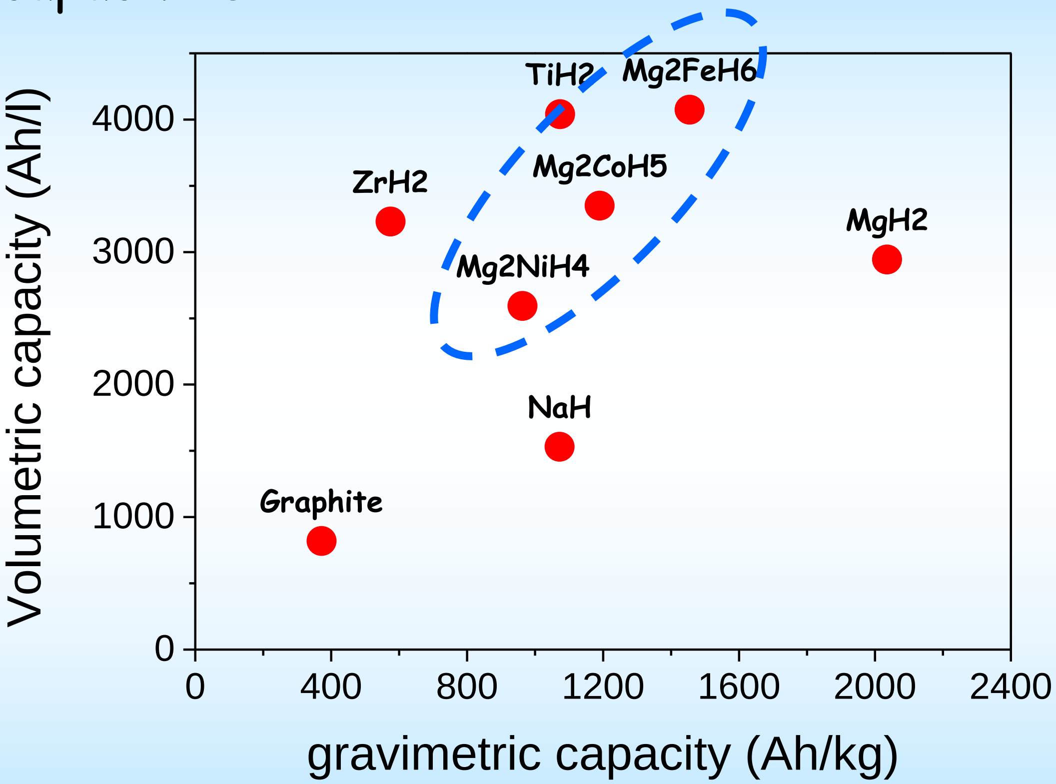
Reversibility concerns (slow kinetics and poor cycle-life) due to:

- Long-range mass transport at RT of Mg, Li and H species
- Reversible breaking and forming of Mg-H and Li-H bonds
- Strong volume changes within the electrode ($\Delta V/V = 83\%$)
- Low electrical conductivity of MgH_2 and LiH phases

Looking for better systems: Mg_2TMH_x compounds

Why are they good candidates?

- Good theoretical capacities

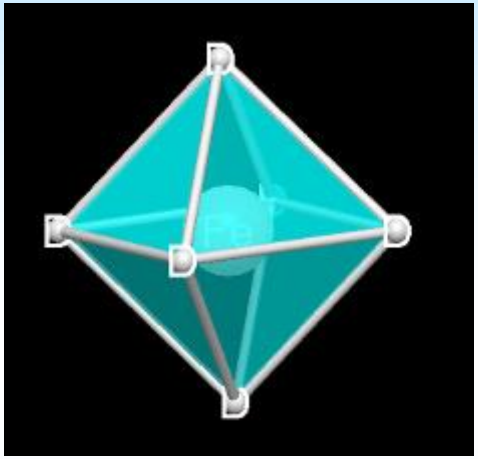


- Transition metals (TM) may create an intrinsic electronic percolation network

Mg_2TM (TM = Fe, Co, Ni) hydrides: synthesis & properties

- Complex hydrides: Covalent TM – H bonding (molecular complex)
  Ionic Mg^{2+} - $[TMH_x]^{4-}$ bonding

Compound	H/M	Cm (wt.% H)	Cv (g_H/l)	T_{dec} (°C)
MgH_2	2	7.66	108	280
Mg_2FeH_6	2	5.47	150	290
Mg_2CoH_5	1.67	4.48	126	320
Mg_2NiH_4	1.34	3.62	98	255

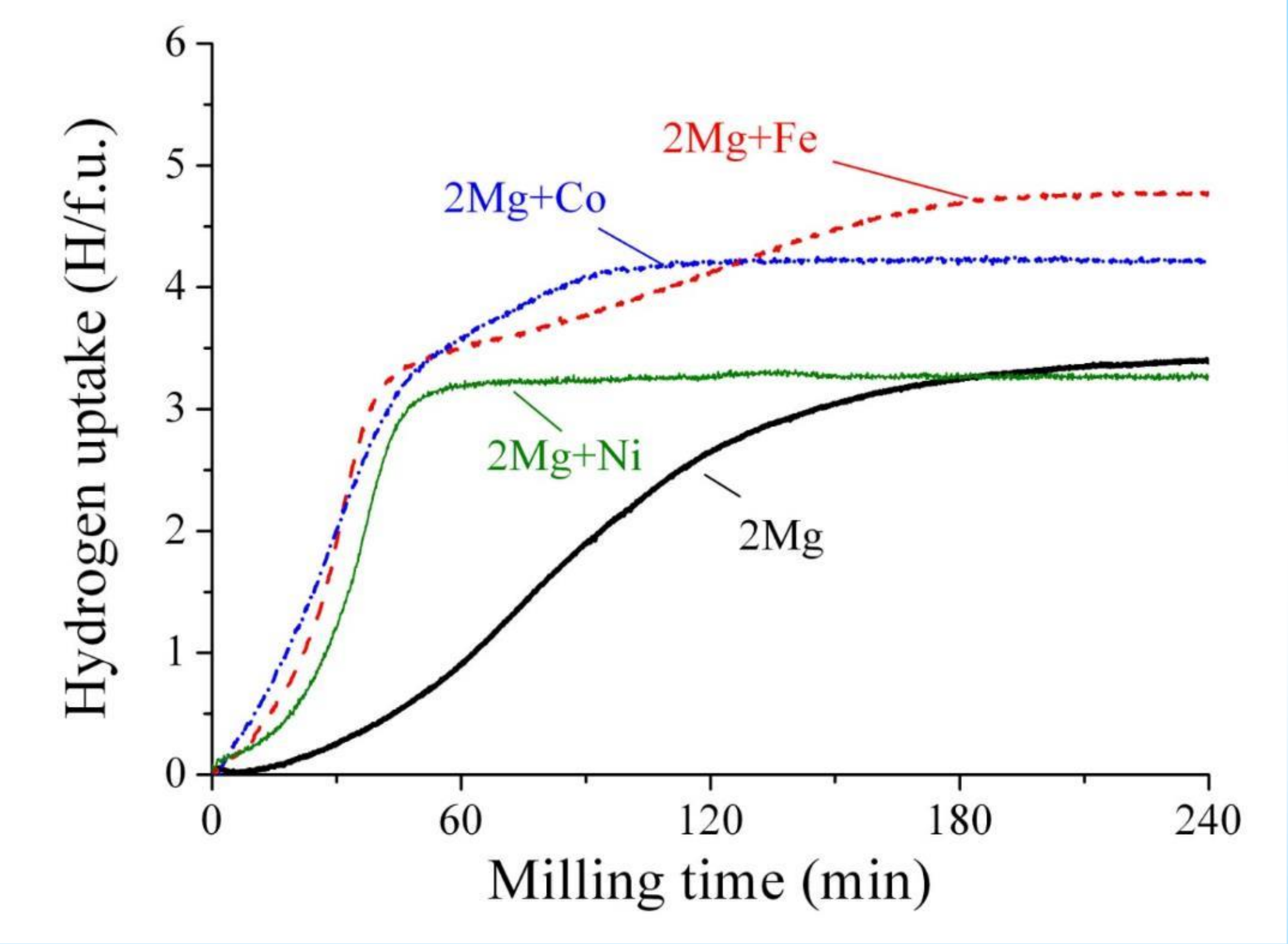


- Classical synthesis: sintering at high pressure and temperature

$$2Mg(s)+Fe(s)+3H_2(g) \xrightarrow[\text{3 days}]{\text{90 bar, 450°C}} Mg_2FeH_6(s)$$

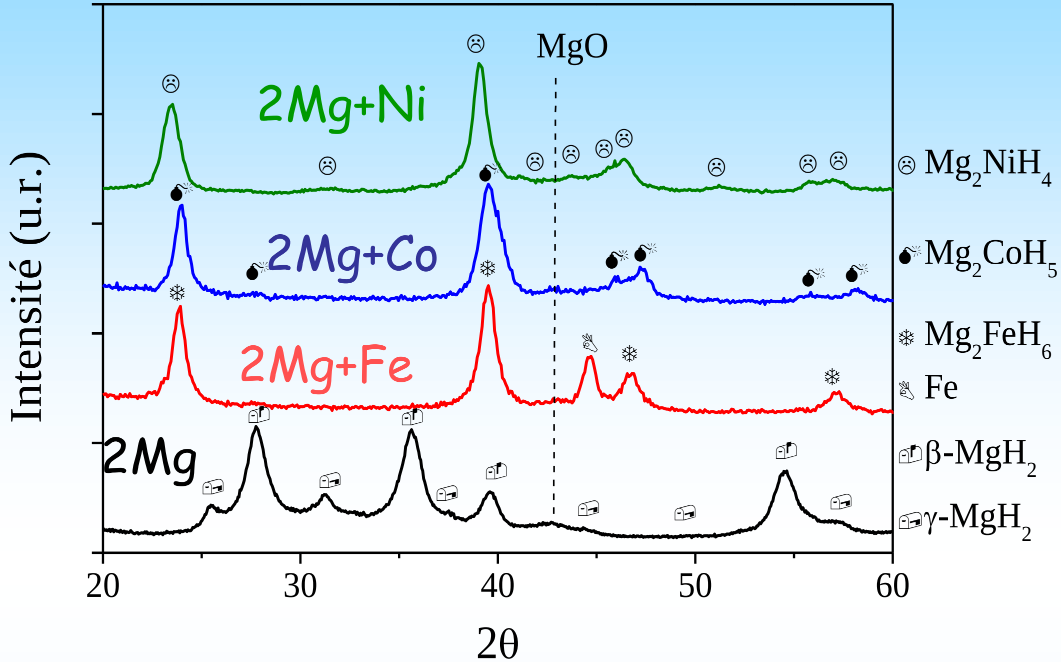
Selvam and Yvon, IJHE 16 (1991) 615

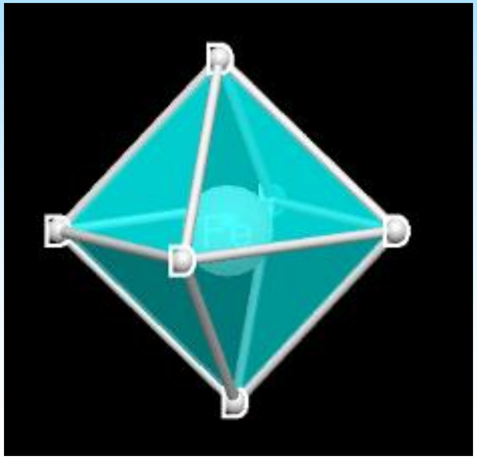
Synthesis by reactive ball milling



Fast compound formation as compared to the classical sintering route

Crystallographic studies of end products



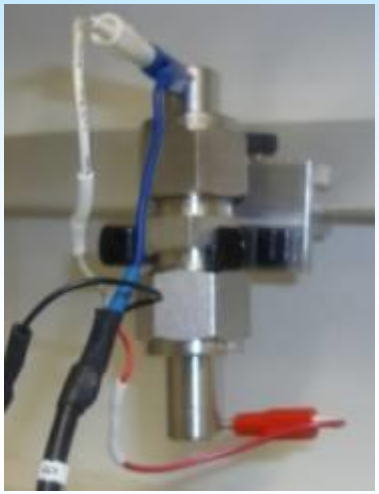


Reactants	Phases	S.G.	Crystallite size
Mg	β-MgH_2 γ-MgH_2	$P4_2/mnm$ $Pbcn$	5 ± 1 nm 3 ± 1 nm
2Mg+Fe	Mg_2FeH_6	Fm-3m	8 ± 1 nm
2Mg+Co	Mg_2CoH_5	$P4/mnm$	8 ± 1 nm
2Mg+Ni	Mg_2NiH_4	$C2/c$	9 ± 1 nm

Electrochemical discharge (galvanostatic mode)

Swagelok half-cells

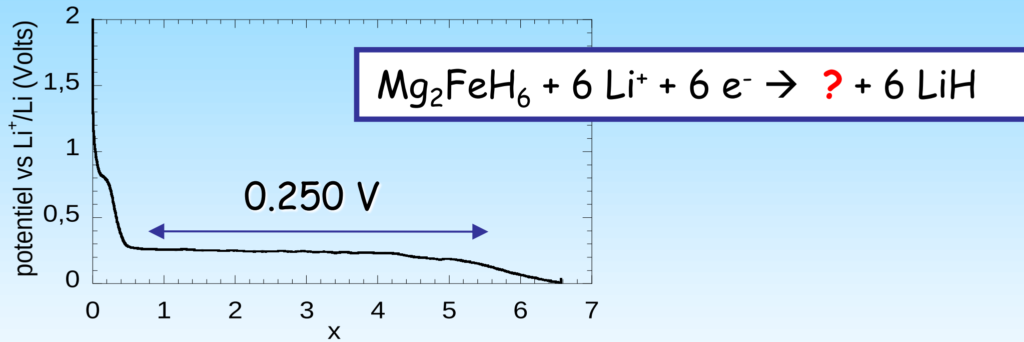
- Li

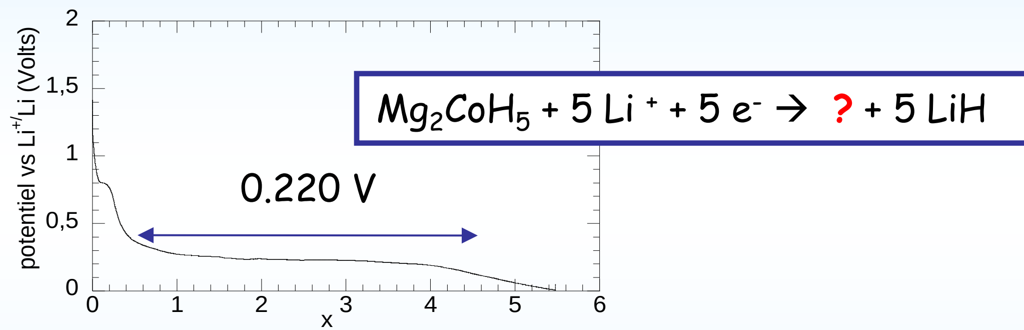


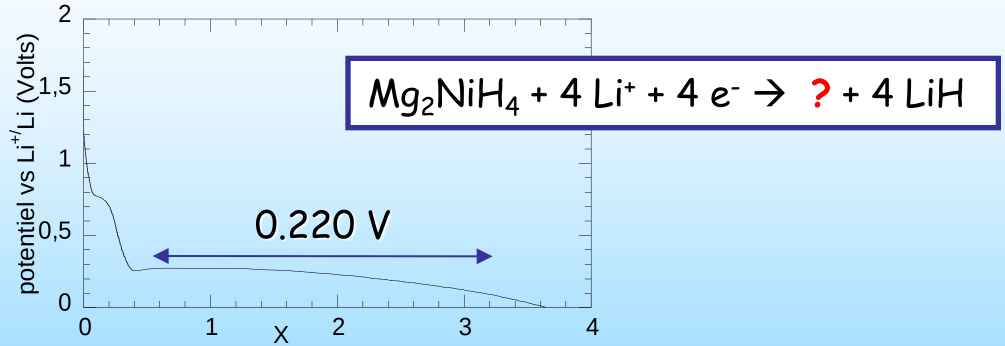
+ Mg_2TMH_X

Electrolyte: LP-30
EC-DMC / 1M $LiPF_6$

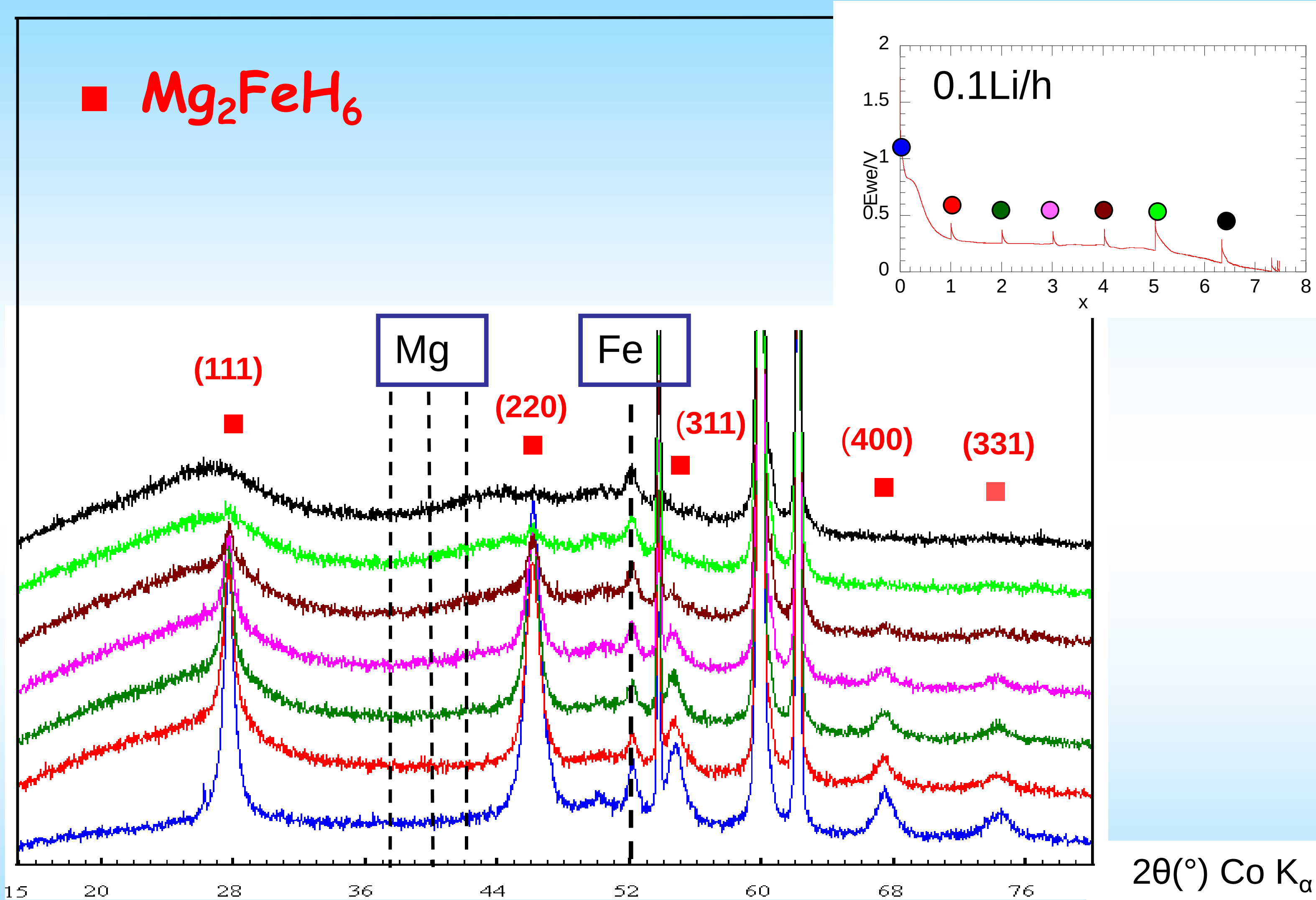
Rate: 0.1 Li/h







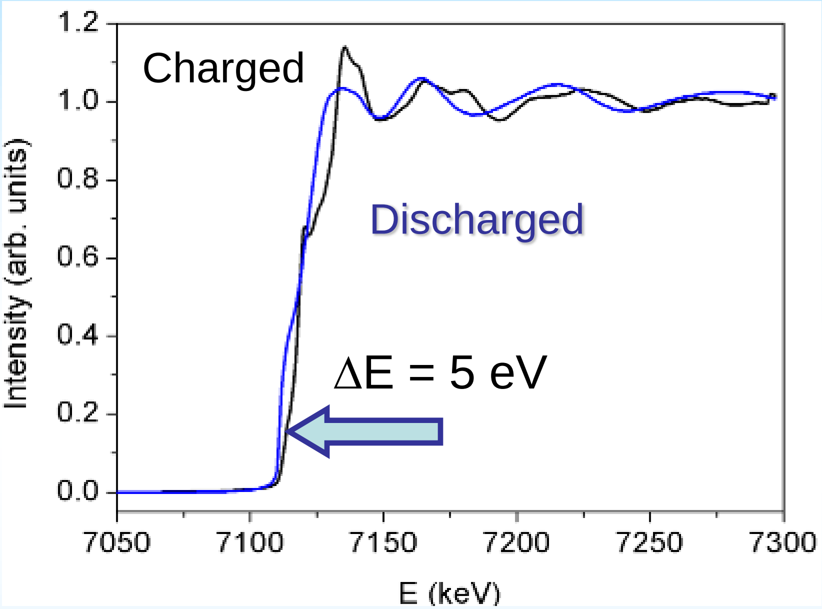
Mg_2FeH_6: In-situ XRD studies (GITT on discharge)



Two-phase transformation : Nano-$Mg_2FeH_6 \xrightarrow{+ 6\,Li^+ + 6\,e^-}$ Amph.-2Mg,Fe (+ 6 LiH)

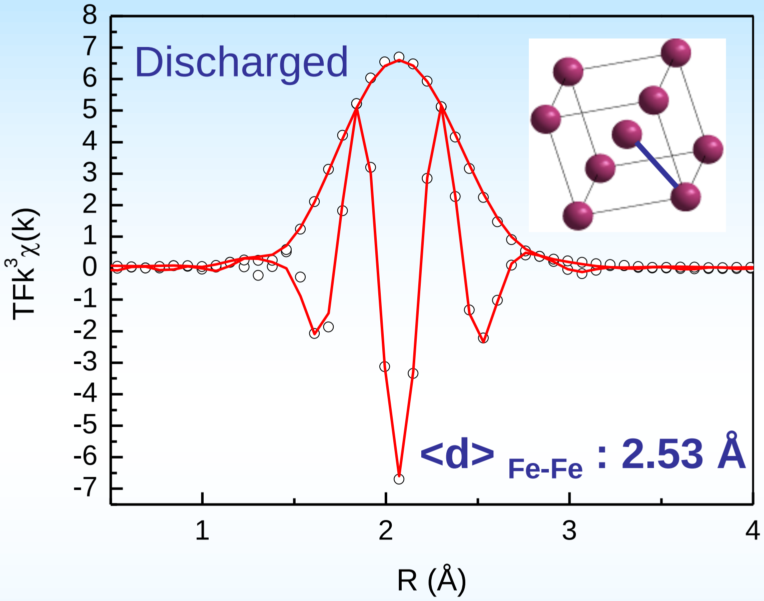
Mg_2FeH_6: EXAFS studies

XANES spectra (Fe-K-edge)



Change of Fe-oxydation state: $Fe^{2+} \rightarrow Fe^0$

EXAFS refinement



Formation of amorphous Fe

- Discharged state: Amorphous Fe and Mg domains + LiH

Conclusions

❖ Nanostructured Mg-based hydrides are efficient materials for energy storage

❖ They can be easily and rapidly synthetized in bulk form by reactive ball milling under H_2 atmosphere

❖ They are excellent materials for reversible hydrogen storage at moderate temperatures and promising candidates for negative electrodes of Li-ion batteries

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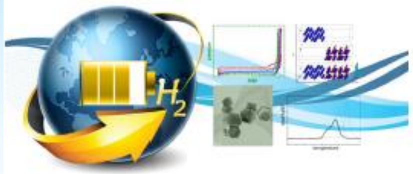

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Thank you for your attention!!!

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