Metal hydrides as hydrogen storage system for fuel cells

Project aim

- Study the possibilities of metal hydrides in hydrogen storage systems for fuel cells.
- Provide a theoretical background for further studies on metal hydrides.
- Study the structures of Magnesium-Nickel hydrides by X-ray diffraction.

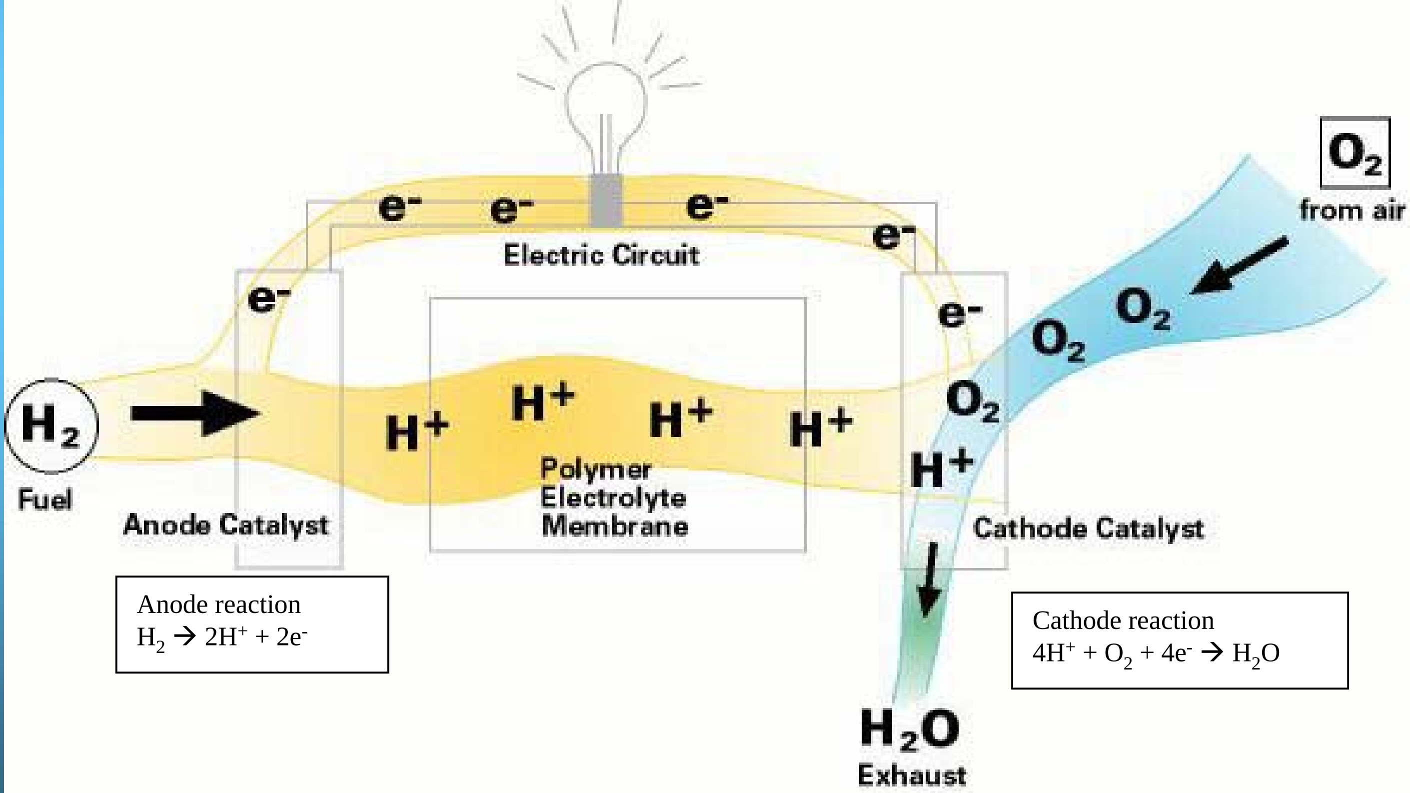
Contents

- Fuel cells
- Hydrogen storage systems
- Metal hydrides
- X-ray diffraction analyses of Mg_2NiH_4 hydrides

Fuel cells

What are fuel cells ?

A electrochemical device that transforms hydrogen and oxygen into electricity, while producing only pure water.



Anode reaction
$H_2 \rightarrow 2H^+ + 2e^-$

Cathode reaction
$4H^+ + O_2 + 4e^- \rightarrow H_2O$

Different types of fuel cells

Fuel cells types	Electrolyte electrode	Working temperatures	Fuel Oxidant	Electrical efficiency
PEMFC Polymer electrolyte membrane FC	Nafion® Electrodes with Pt	30 - 80°C	pure H_2 Air or pure O2	~ 35%
AFC Alkaline FC	KOH concentrate carbon Electrodes with Pt, Ag catalyst	60 - 100°C	pure H_2 Air or pure O_2	~ 35%
PAFC Phosphoric acid FC	H_3PO_4 concentrate Electrodes with Pt	~ 200°C	H_2, CH_4, CH_3OH Air	~ 40%
MCFC Molten carbonate FC	Molten carbonate, Li_2CO_3/ Na_2CO_3 nickel Electrodes	~ 650°C	H_2, CH_4 Air	~ 50%
SOFC Solid oxide FC	Ceramic solid oxide nickel Electrodes and ceramic solid oxide	~ 1000°C	H_2, CH_4, CH_3OH Air	~ 55%

Fuel cell applications

- Stationary electric power generators.
  To provide reliable, clean, high quality electricity.

- Portable Power.

- Transportation applications.
  Efficient and clean engines for the future's vehicles.

Hydrogen storage systems

Hydrogen storage systems

- Hydrogen contains more chemical energy per weight than any hydrocarbon fuel, but it is also the lightest existing substance and therefore problematic to store effectively in small containers.
- Hydrogen storage technologies must be significantly advanced if a hydrogen based energy system, particularly in the transportation sector, is to be established.
- Target values (US DOE Hydrogen Program):
  - 62 kg H/m^3
  - 6.5 wt% (grams of hydrogen per gram of system weight)

Hydrogen storage systems

Available hydrogen storage systems:

- Compressed hydrogen (CGH_2)
- Liquefied hydrogen (LH_2)

Promising hydrogen storage systems:

- Carbon nanostructures
- Hydride slurry
- Metal hydrides

Hydrogen storage systems

SYSTEM	TECHNICAL PARAMETERS	VOLUME INCL. CONTAINMENT (l)	WEIGHT (kg)	WEIGHT INCL. CONTAINMENT (kg)
Methane (CH_4)	300 bar	82	20	46
Gasoline	Liquid	~40	~30	~33
CGH_2 (Compressed gas)	300 bar 700 bar	310 180	5 5	65 84
LH_2 (Liquid hydrogen)	20.8 K	150	5	56
Metal hydrides	2%-weight 3%-weight	128 85	258 172	284 189
Carbon adsorption	5%-weight 10%-weight	100-300 50-150	105 55	115 60

5 kg of stored hydrogen are assumed enough to run a car with 0.3 kWh/km consumption for about 500 km.

Compressed hydrogen (CGH_2)

- The only commercially available method for ambient-temperature hydrogen storage for vehicle applications.
- Storage capacities depending on the container used:

Container	Volumetric storage density (kg/m^3)	Gravimetric density (wt%)
Fiberglass-wrapped aluminum	12	2
Carbon fiber-wrapped polymer	15	5
Lightweight pressure vessels		12 (expected)

Liquefied hydrogen (LH$_2$)

- Stored as a cryogenic liquid without the need for pressurization cooling hydrogen to below the boiling point of -252.7 °C .

- LH$_2$ is stored in small tanks of 100 l to up to stationary spherical tanks of some 2000 m^3. All tanks have a vacuum-insulation between inner and outer wall of the tank system.

- Main problem → evaporation of LH$_2$ into GH$_2$:

Large volume stationary tanks (several 100 m^3 to several 1000 m^3):	0.1% per day
Mobile cylindrical delivery tanks (38 to 55 m^3):	1%
Small vehicle storage tanks (about 100 l to 400 l):	1.7% - 3%

Carbon nanostructures

- Still at a research level and not yet mature for industrial application → not comparable at the same level as metal hydrides or other established storage technologies.

- Inherently safe and potentially high energy density hydrogen storage method that could be extremely energy efficient.

Carbon adsorption methods

- **Carbon nanofibers**
  - Produced by decomposition of mixtures of ethylene, hydrogen and carbon monoxide on selected metal and alloy catalysts.
  - Maximum experimental value of 1.52 wt% at ambient temperature and 125 atm.
  - Fiber quality and rate of growth are extremely sensitive to growth temperatures, gas composition and the exact crystal structure, shape, size, purity and uniformity of the catalyst particles

Carbon adsorption methods

- **Multi-wall carbon nanotubes (MWNT)**
  - Layers of nested concentric cylinders of graphite with a hollow center.
  - Storage capacity of 2.5 wt% for Li-doped MWNTs.

- **Carbon single-wall nanotubes (SWNT)**
  - Sheet of graphite that is wrapped to meet itself forming a single elongated and seamless tube. Individual tubes self-assemble during synthesis form bundles that contain hundreds of SWNTs.
  - Storage capacity of 7 wt% at laboratory scale.

Hydride slurry

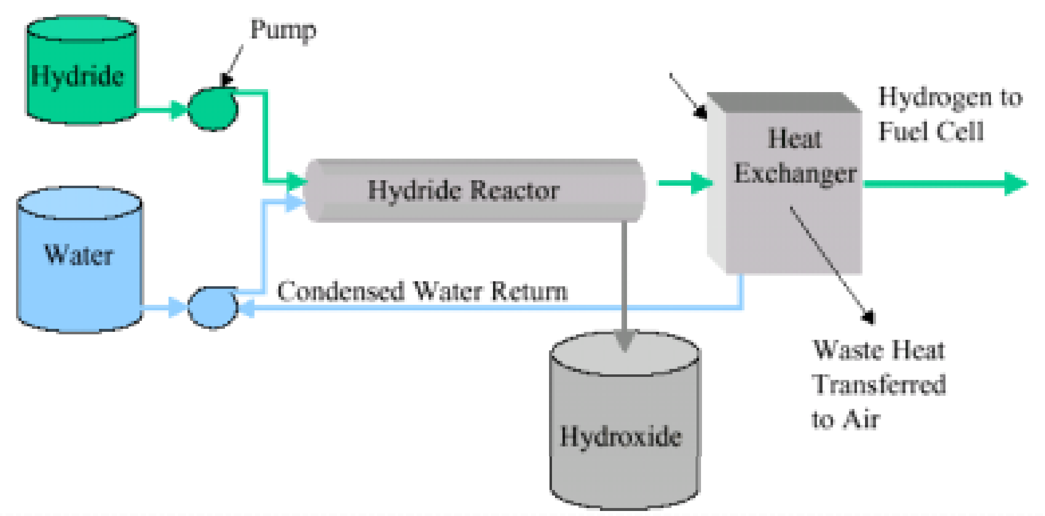
- When chemical hydrides are mixed with water they produce hydrogen:

Chemical Reaction	**Gravimetric Density, wt%** (Hydride only)
$CaH_2 + 2\,H_2O \Rightarrow Ca(OH)_2 + 2\,H_2$	9,6
$MgH_2 + 2\,H_2O \Rightarrow Mg(OH)_2 + 2\,H_2$	15,3
$LiH + H_2O \Rightarrow LiOH + H_2$	25,2
$LiBH_4 + 4\,H_2O \Rightarrow LiOH + H_3BO_3 + 4\,H_2$	37,0
$NaBH_4 + 4\,H_2O \Rightarrow NaOH + H_3BO_3 + 4\,H_2$	21,3

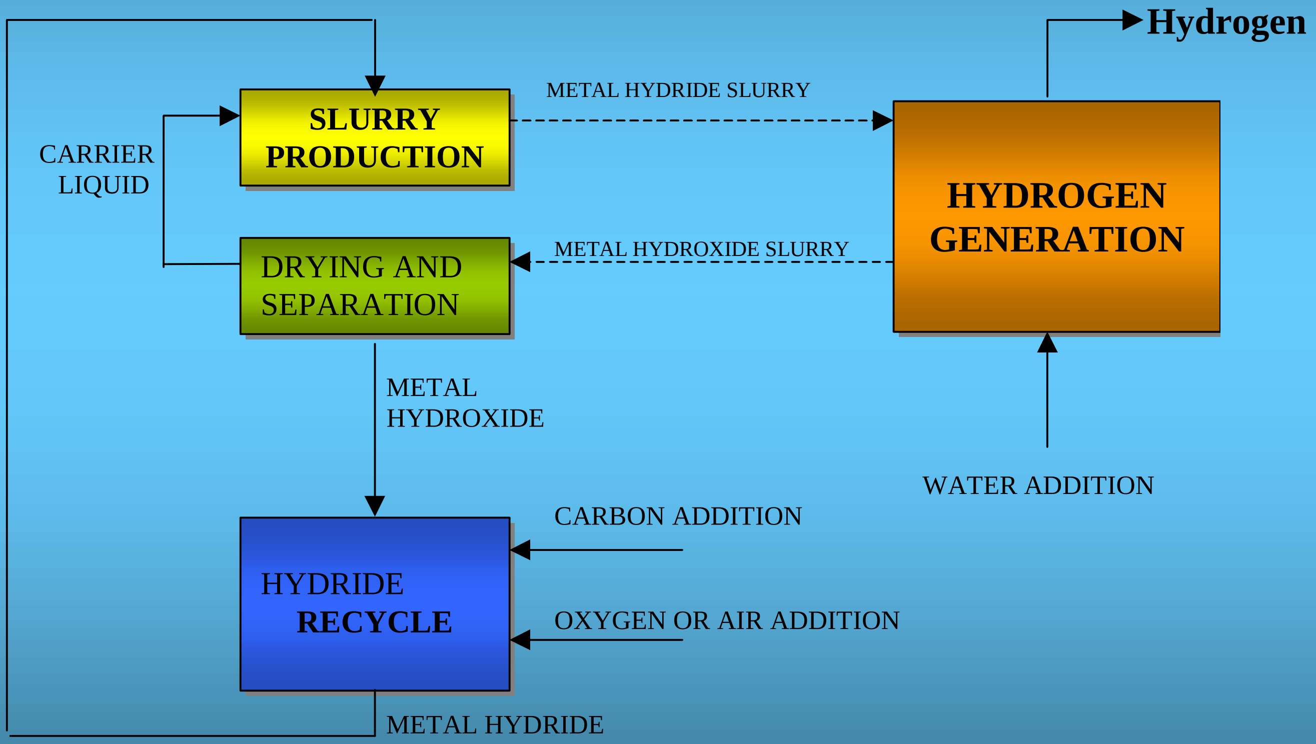
- Hydride slurry: mixture of fine, solid metal hydride particles and a liquid (normally a mineral oil) to make a pumpable mixture.

Hydrogen generation system

- Hydride slurry and water are pumped into the reactor at one end.
- Hydrogen and water vapor are separated from the hydroxide product in the head of the hydroxide tank.
- Water vapor is condensed in the heat exchanger. Condensed water is returned to the water circuit



Transmission/storage process



Metal hydrides

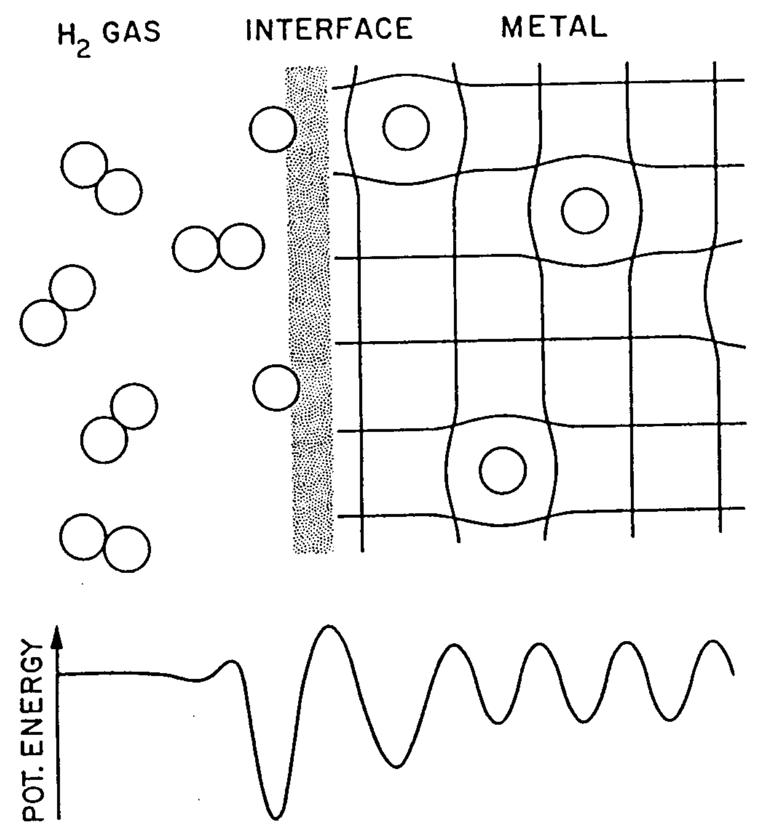
Reversible Metal-H_2 gas reaction

$$M + (x/2)H_2 \rightleftarrows MHx$$

Hydrides store only about 2% to 7% hydrogen by weight, but have high volumetric storage densities. The storage density is higher than liquid or solid hydrogen.

Material	**H-atoms pr. cm^3 (x10^{-22})**	**Weight pct**
H_2 gas (200 bar)	0,99	100
H_2 liquid (20 K)	4,2	100
H_2 solid (4,2 K)	5,3	100
MgH_2	6,5	7,6
Mg_2NiH_4	5,9	3,6
$TiFeH_2$	6	1,89
$LaNi_5H_6$	5,5	1,37

General mechanism of H_2 absorption



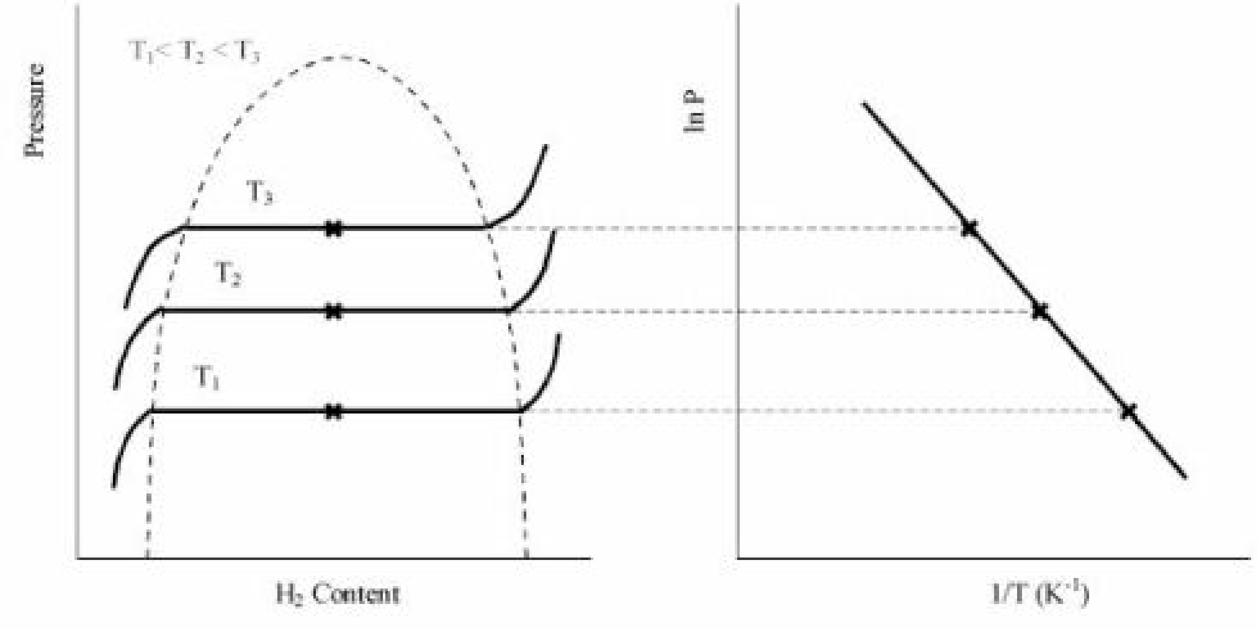
Under hydrogen pressure, hydrides absorb hydrogen and release heat.

By reducing the pressure and supplying heat, the hydrogen is released.

The H_2 molecule is first absorbed on the surface and then dissociated as strongly bound, individual H atoms.

Phenomenology and thermodynamic

Pressure Composition isotherms

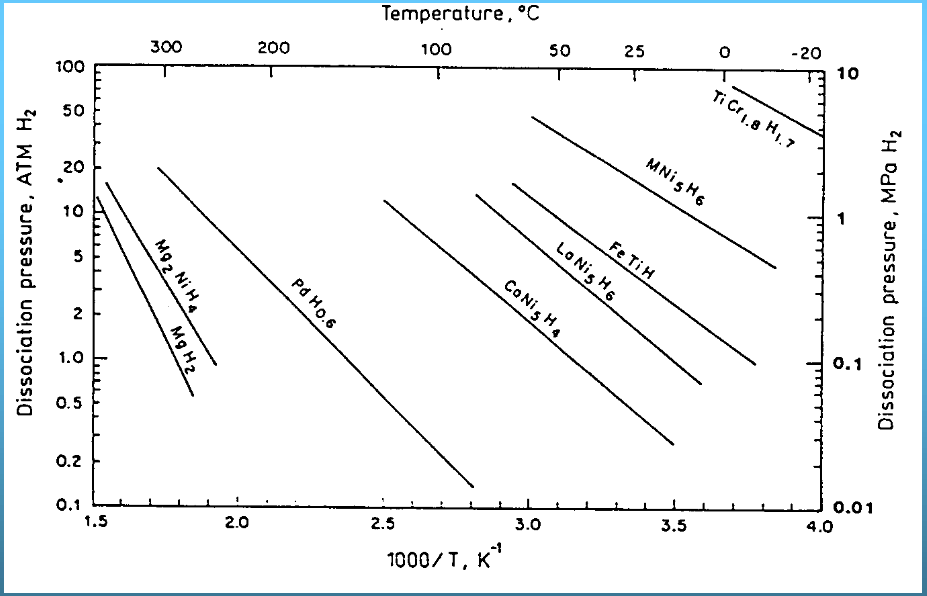


Phenomenology and thermodynamic

Van’t Hoff equation :

$$\ln p = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

Van’t Hoff Plots :



Which metal hydrides for hydrogen storage ?

Many parameters :

- Weight
- Temperature and pressure of hydriding/dehydriding
- Hydrogen capacity and amount of usable hydrogen
- Rate of absorption/desorption
- Cyclic stability
- Cost and availability.

Which metal hydrides for hydrogen storage ?

There are two important types of hydrides:

- Intermetallic Compound hydrides (IMC hydrides)
- Complex hydrides

In IMC hydrides H_2 storage capacity varies from 1 to 7,6 wt.% depending on the metals selected.

However at low temperature (around 150°C), storage capacity doesn’t excess 2 wt.%

→ Greater promise lies in the ways to synthesize alloys (nanoparticles)

Which metal hydrides for hydrogen storage ?

There are two important types of hydrides:

- Intermetallic Compound hydrides (IMC hydrides)
- Complex hydrides

In complex hydrides, high hydrogen content (5 to 8 wt.% can be obtained. However the M-H bonding is very strong, the hydrides are very stable and rate of hydrogen release is very slow.

→ Greater promise lies in catalyzed hydride complexes (with Ti or Zr catalyst)

Which metal hydrides for hydrogen storage ?

The best metal hydride can be chosen by the operating temperature :

at 150°C, Very interesting behavior have been found in catalyzed complex **sodium alanate** (NaAlH4) with reversible H2 capacity of 5 wt.%

Around 200°C, **catalyzed lithium based complex** hydrides can be used with 7 wt.% H_2 capacity

Above 250°C, **Magnesium based hydrides** are the best solution. H_2 capacity is about 7 wt.%, in addition, row material is cheap and the hydride is easy to produce

X-ray diffraction analyses of Mg_2NiH_4 hydrides

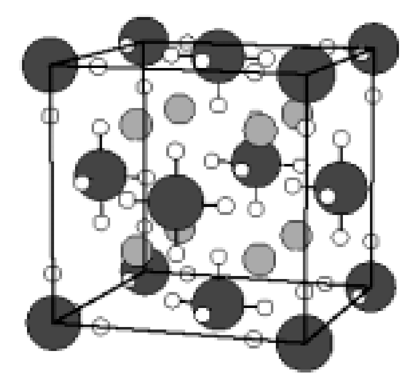
Mg_2NiH_4 hydride

- Mg_2NiH_4 is one of the most promising metal hydrides for future hydrogen storage and for increasing the negative electrode capacity in the nickel metal hydride (NiMH) batteries.
  - ➘ Dehydriding temperature is about 520 – 570 K, which is a little too high for fuel cell application.
  - ➘ Desorption of hydrogen by electrochemical splitting of H_2O is too slow at room temperature.

➡ To obtain a suitable material for practical hydrogen storage it is necessary to improve our knowledge on Mg_2NiH_4

High-temperature phase (HT)

- Above 235°C a cubic high-temperature phase (HT) of Mg_2NiH_4 exists with a=6.490 Å.

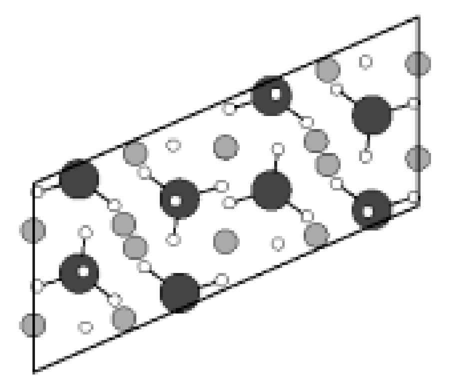


The magnesium ions form a cube around the $[NiH_4]$-complex.

The hydrogen atoms perform a rapid reorientational motion around the central nickel atom

Low-temperature phase (LT)

Unit cell parameters of the monoclinic low-temperature phase:
a=14.343 b=6.4038 c=6.4830 Å β=113.52°



The motion of hydrogen around the central atom is frozen.

Frequently a stacking fault on unit cell level is introduced into the lattice: **microtwinning**

- **LT1** (without microtwinning)
- **LT2** (with microtwinning)

Phase transformation

- LT-HT phase transformation is believed to occur at 235°C.
- By high temperature resistivity measurements a conducting – insulating transition is observed at 200°C for LT1 pressed samples. For LT2 pressed samples, this transition occurs around 180°C.
- This temperature is probably correlated to a change in the structure, for example introduction of microtwinning into the lattice, or to LT-HT transition.

➡ **In situ X-ray diffraction** experiments should be made to investigate what happens

Experimental

- Samples:
  - LT1
  - LT2

- Two heating and cooling cycles:

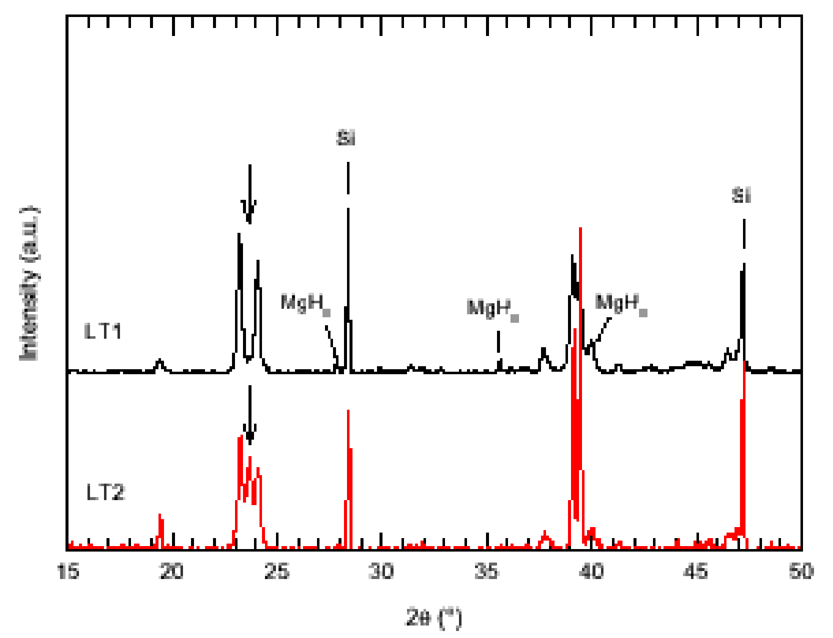
Ambient temperature (20°C) ⇒ 210°C ⇒ 146°C ⇒ 210°C ⇒Ambient temperature

- Air atmosphere

LT1 and LT2 X-ray diffraction profiles

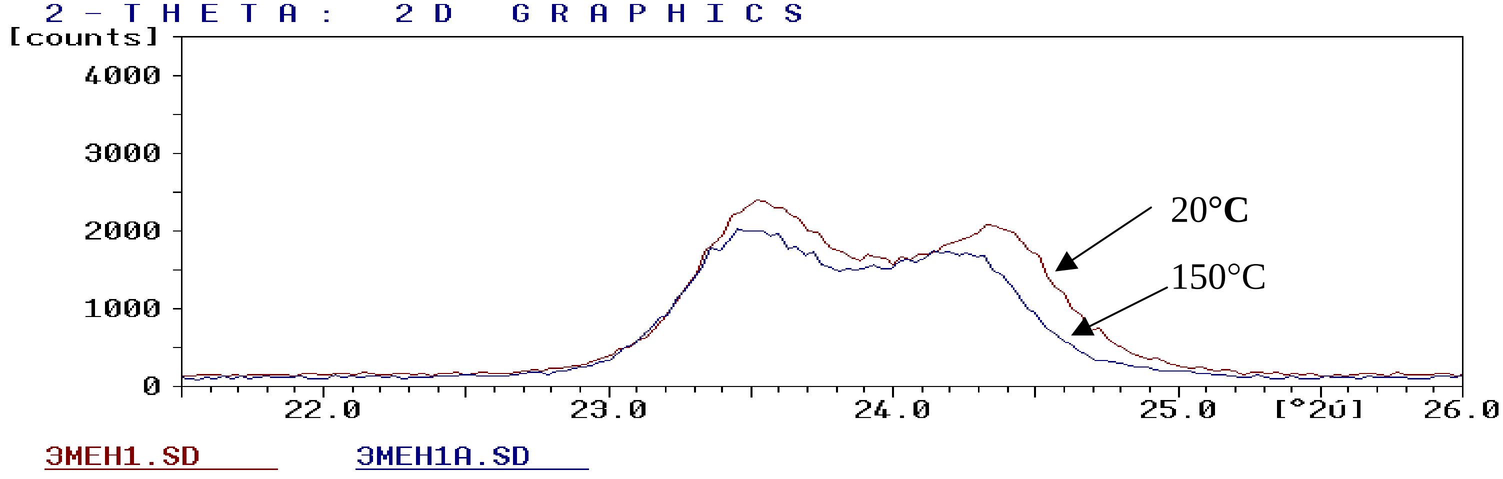
•Existence of some extra peaks in the pattern of the LT2 modification.

•The strongest one, at 2θ=23.7°, is believed to be attributed to microtwinning in the hydride lattice

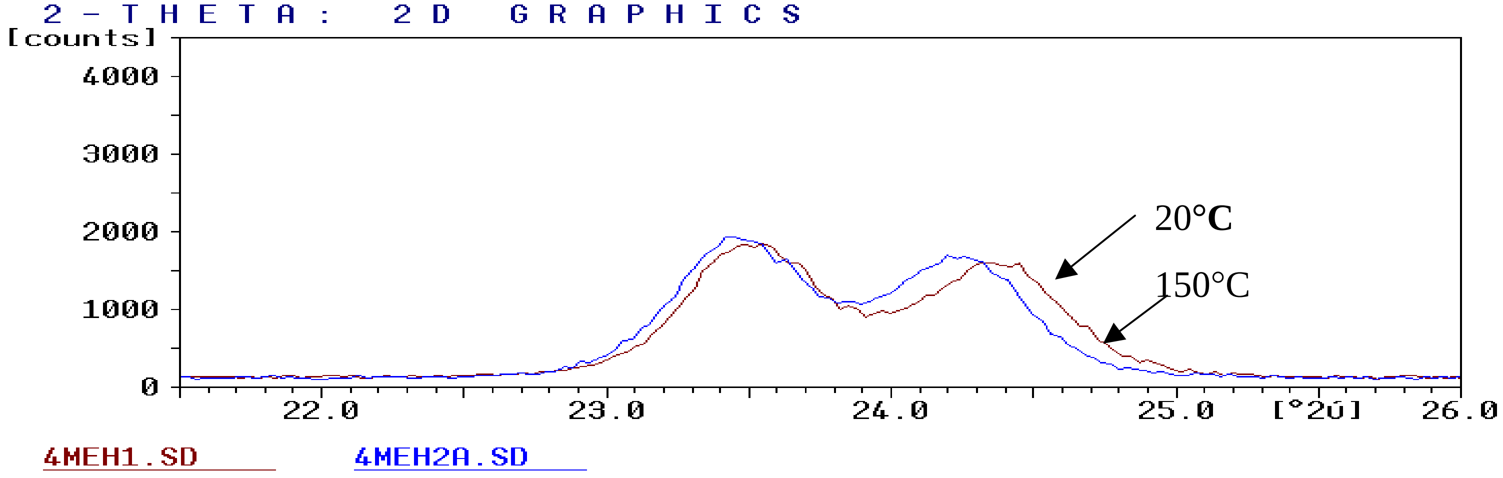


X-ray patterns at 20°C

LT2

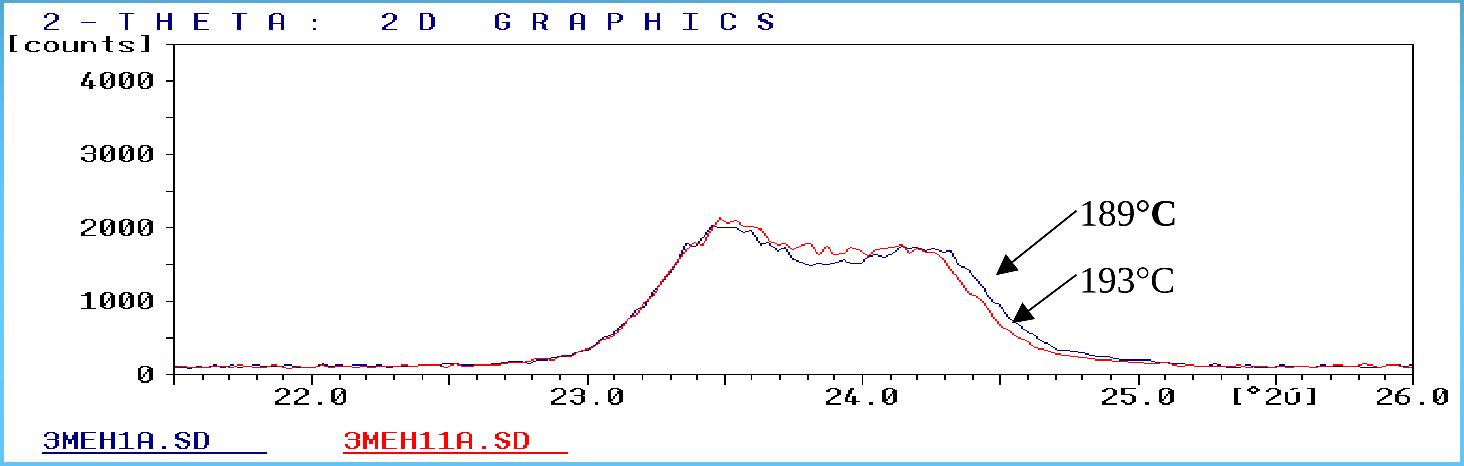


LT1



Beginning of the phase transition

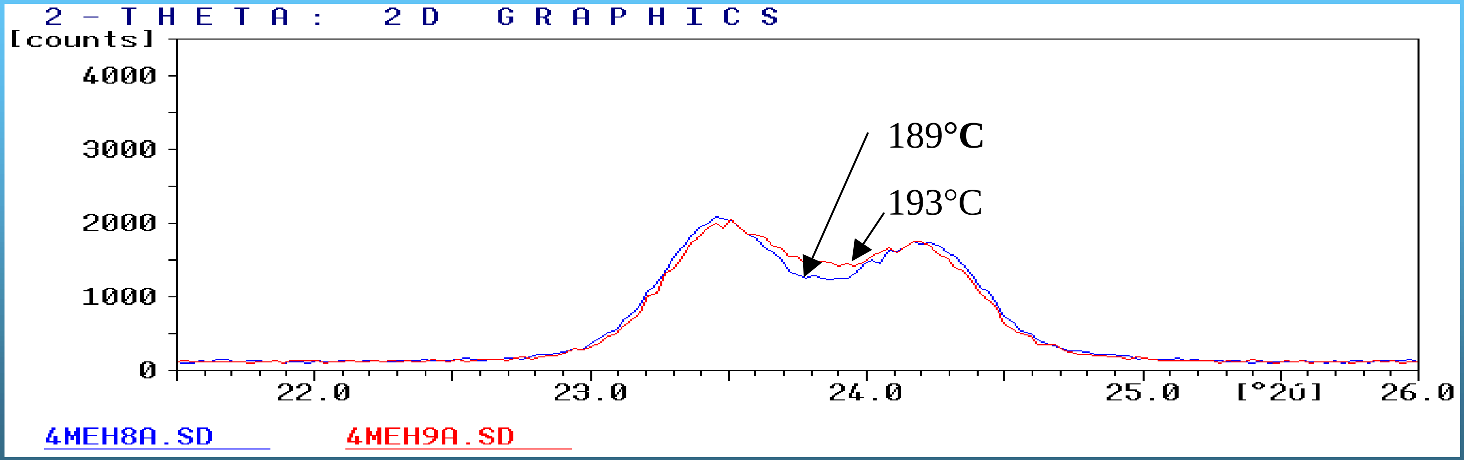
LT2



189°**C**

193°C

LT1

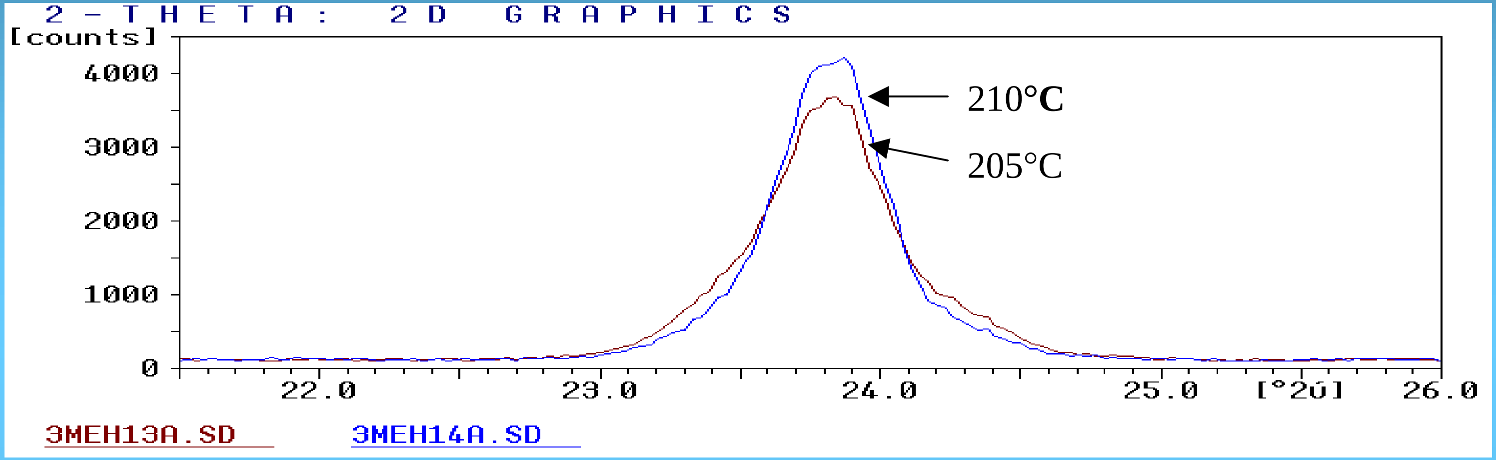


189°**C**

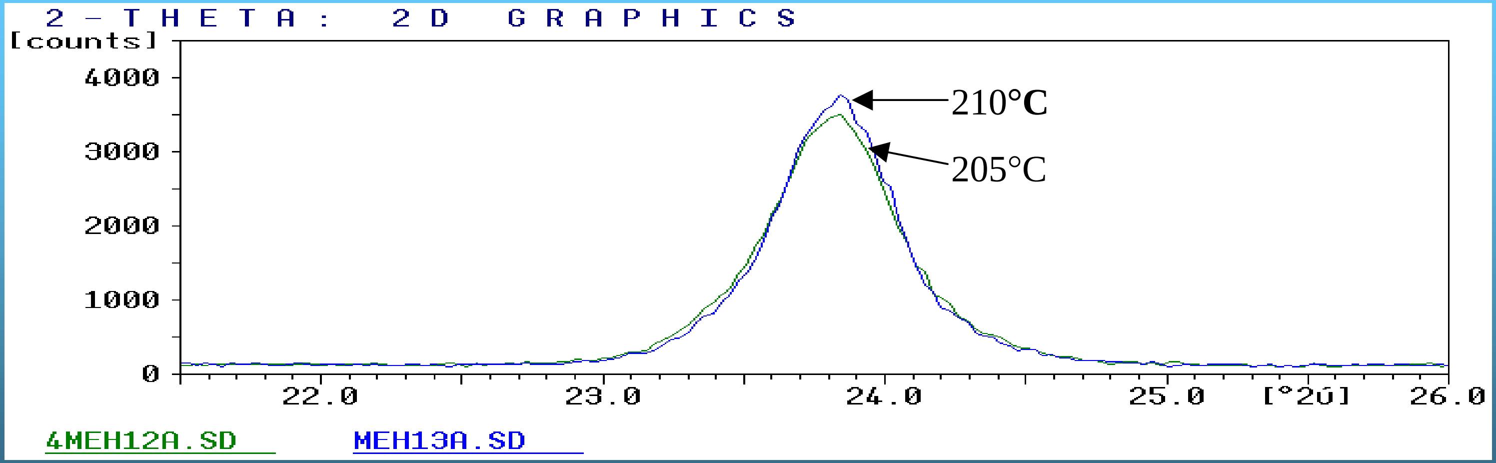
193°C

End of the phase transition

LT2

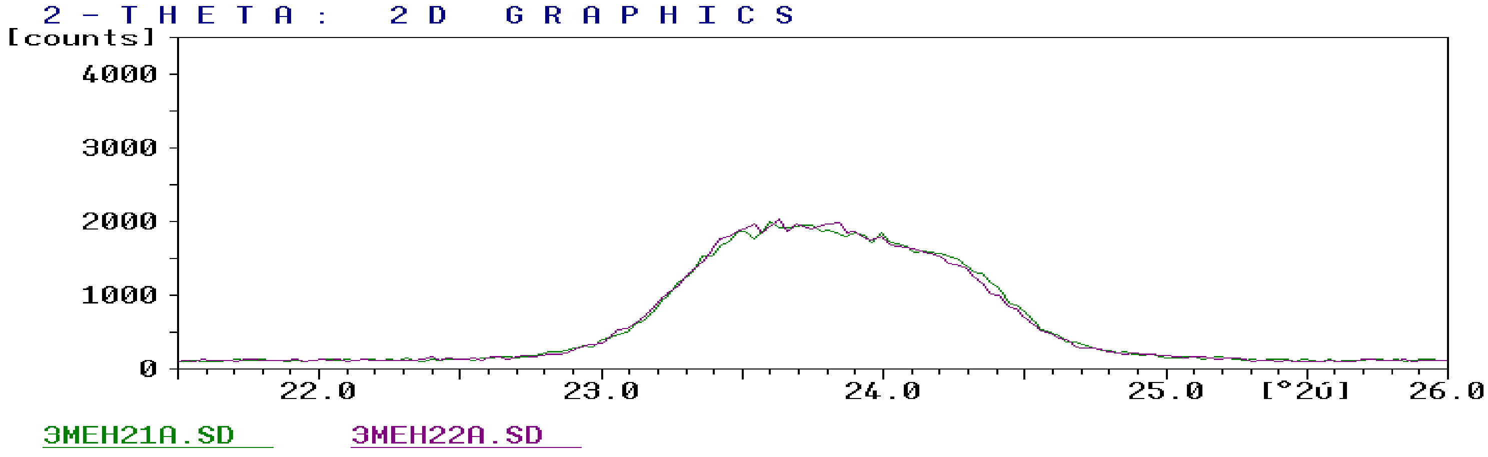


LT1



X-ray patterns after cooling

LT2



LT1