International Hydrogen Storage Conference

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NUOVE TECNOLOGIE,
L'ENERGIA E L'AMBIENTE

Approaching DOE hydrogen storage long-term goals

P.P. Prosini, C. Cento, M. Conte, P. Gislon, M. Brocco

IDROCOMB-ENEA

Lucca, June 20, 2005

Hydrocarbons represent the only way to power automobiles.

How can we move without gasoline?

The negative impact.
Hydrocarbons are very polluting agents

- **The prospective of sharing another decade with hydrocarbon combustion products from automobile engines**

  IS NOT ACCEPTABLE !

Hydrogen-fuelled automobiles (H-Cars)

Roughly speaking, a performing H-Car burns 1 kg of hydrogen per 100km

- To meet the market request

5 kg hydrogen must be

stored in the car.

- To meet the DOE

technical target….

We focus our attention on four long-term targets

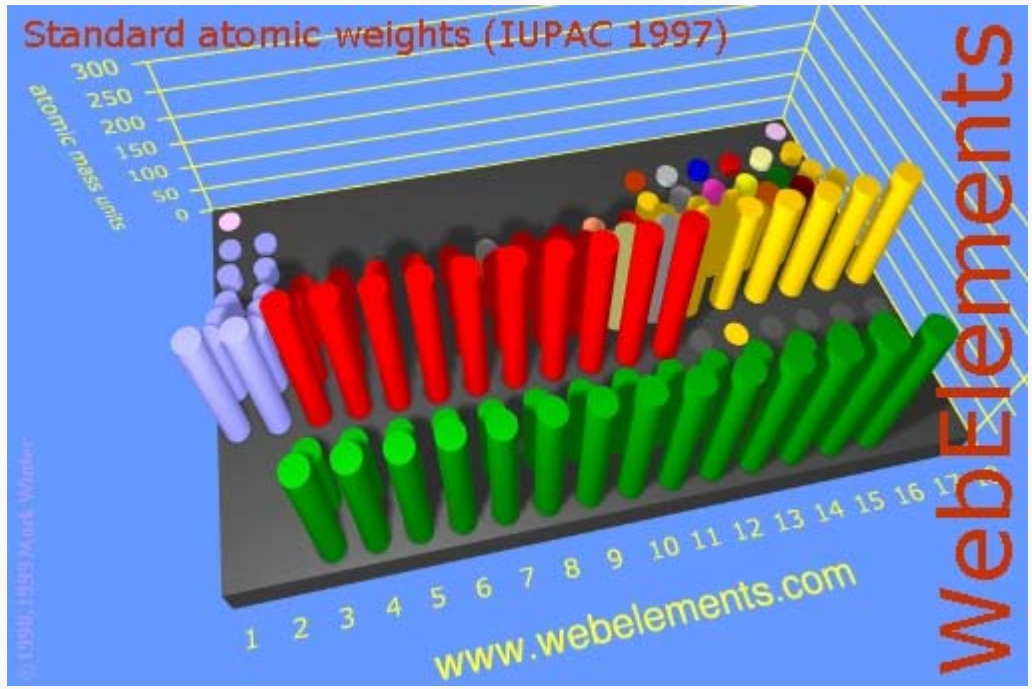
Table 1. DOE Technical Targets: On-Board Hydrogen Storage Systems[a, b, c]

Storage Parameter	Units	2007*	2010	2015
Usable, specific-energy from H_2 (net useful energy/max *system* mass)[d] ("Gravimetric Capacity")	kWh/kg (wt.% hydrogen)	1.5 (4.5%)	2 (6%)	3 (9%)
Usable energy density from H_2 (net useful energy/max *system* volume) ("Volumetric Capacity")	kWh/L (kg H_2/L)	1.2 (0.036)	1.5 (0.045)	2.7 (0.081)
Storage system cost[e]	$/kWh net ($/kg H_2)	6 (200)	4 (133)	2 (67)
System Fill Time for 5-kg hydrogen	min	10	3	2.5

Solid metal hydride

To meet DOE goals a metal hydride should have:

1. **Low molecular weight and/or high hydrogen content**
2. **High density**
3. **Low reaction enthalpy**
4. **Low cost**



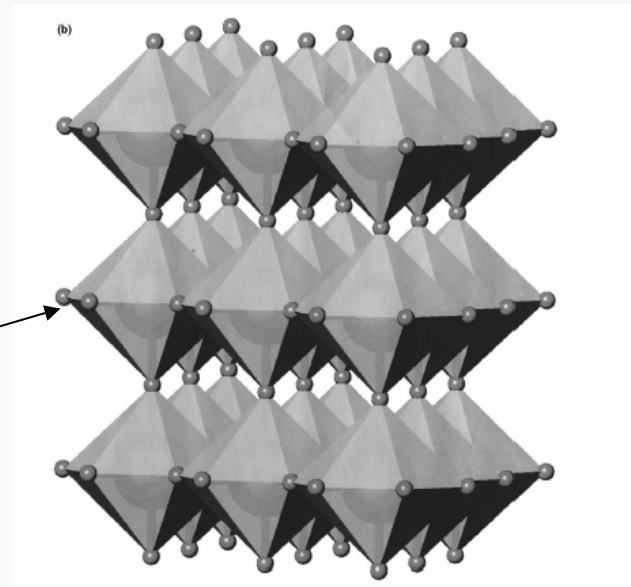
The case of Li_3N

$Li_3N + H_2 \rightarrow LiH + Li_2NH$ 5.7 wt.% H_2

*$Li_2NH + H_2 \rightarrow LiH + LiNH_2$ 5.5 wt.% H_2

We found that 2 mol % Ti doped Li_3N reacts with hydrogen at 285°C and 30 bar following the below equation

$Li_3N + 2H_2 \rightarrow 2LiH + LiNH_2$ 11.2 wt.% H_2

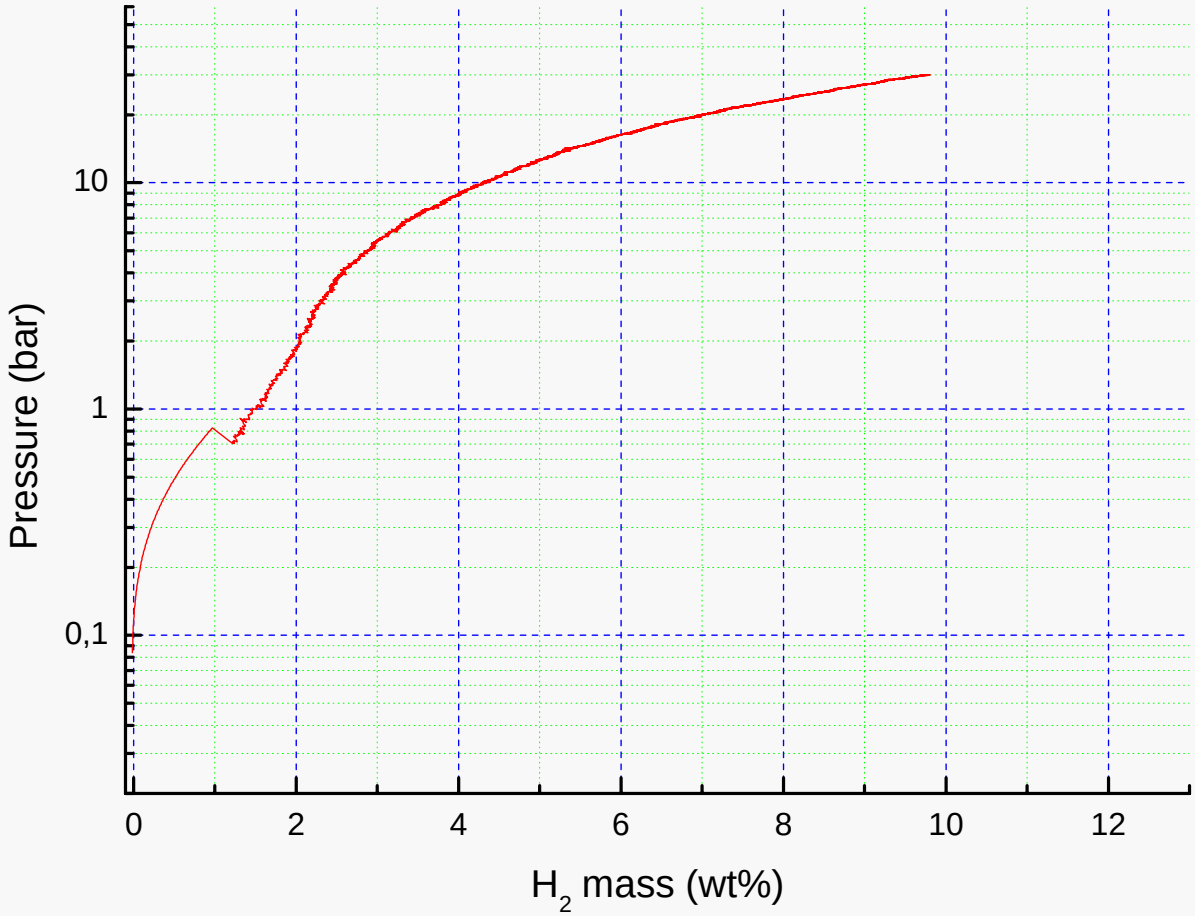


Crystal structure of Li3N

* P. Chen et al., Nature, vol. 420, 21 November 2002.

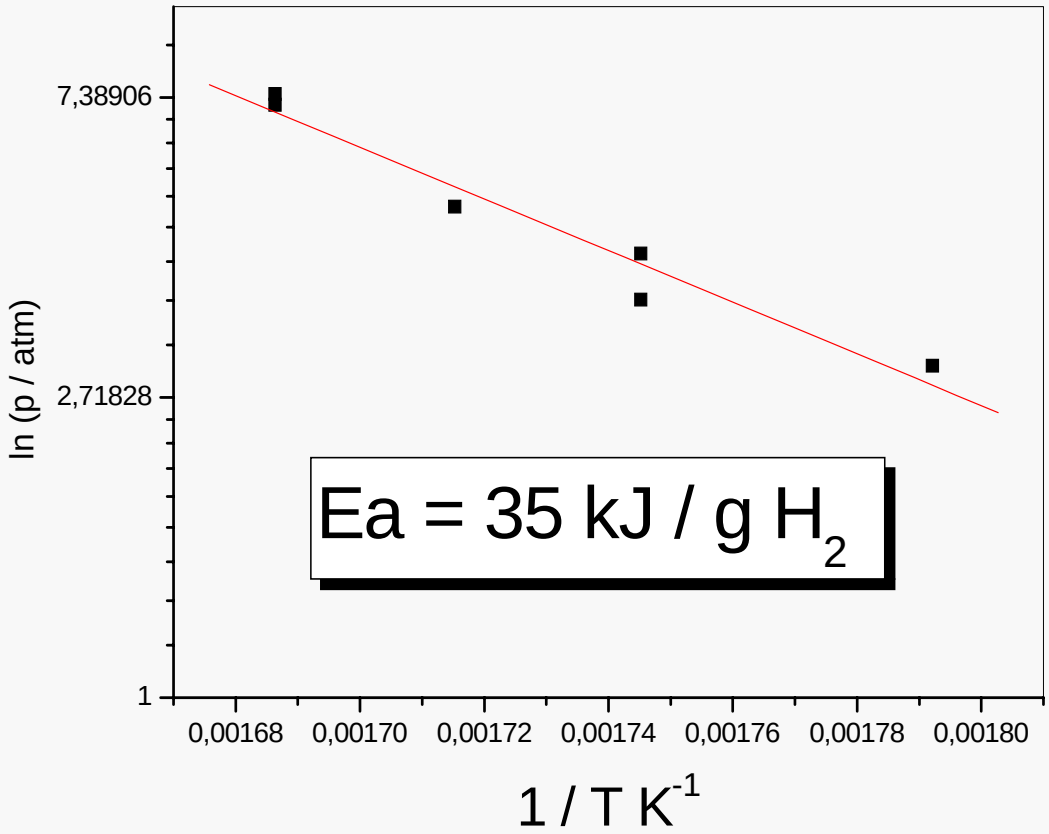
Pressure vs. composition isotherm at 258°C

About 10.0 wt. % H_2 was reversibly desorbed at 285°C



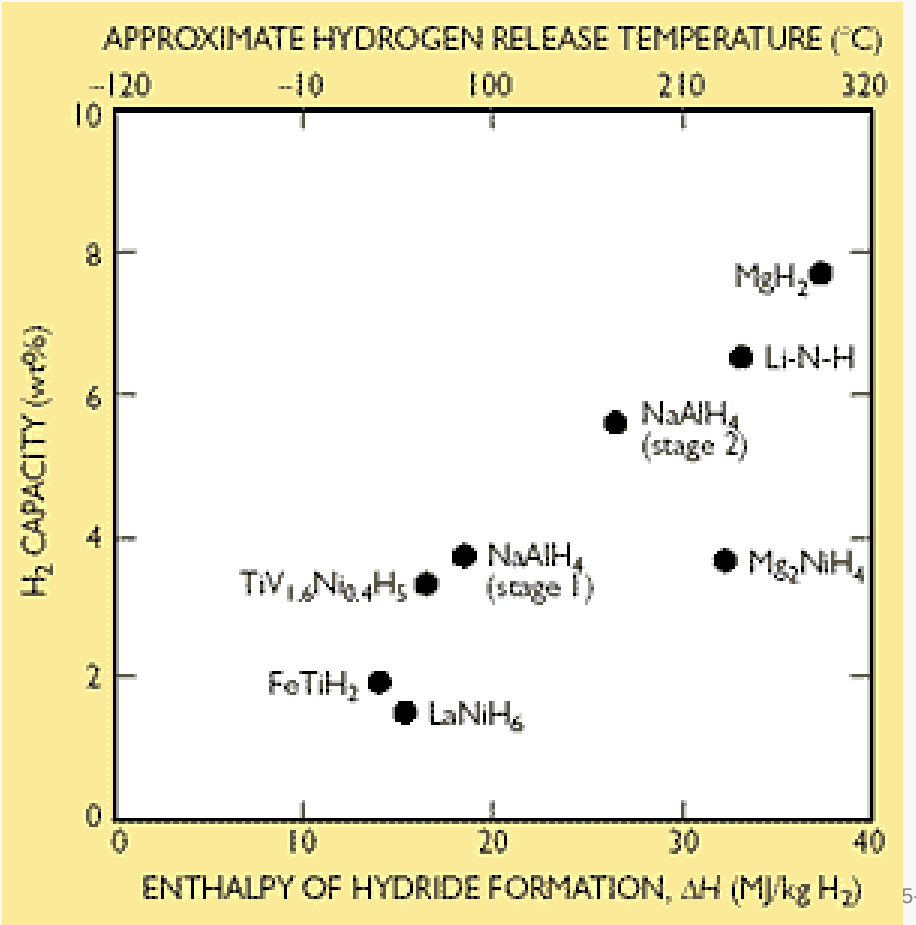
$Li_3N+C_{16}H_{36}O_4Ti$ P_{max}=30bar, Flow=20ml/min, Temp=285°C,

The enthalpy of reaction was 35 kJ per g H_2



The high enthalpy has several important consequences

- Working temperature is relatively high (285°C)
- Part of the hydrogen has to be “burned” to provide the heat for hydrogen desorption.
- This parasitic reaction can reduce the hydrogen content to about 70% of the stored one.
- The hydrogen storage capacity is reduced to 7.0 wt. %.



High enthalpy strongly increases the fill time.

- Technological challenges are the fabrication of high temperature tanks able to exchange heat quickly.
- About 1 MW of heat should be disposed in a 2.5 minutes fast refill.

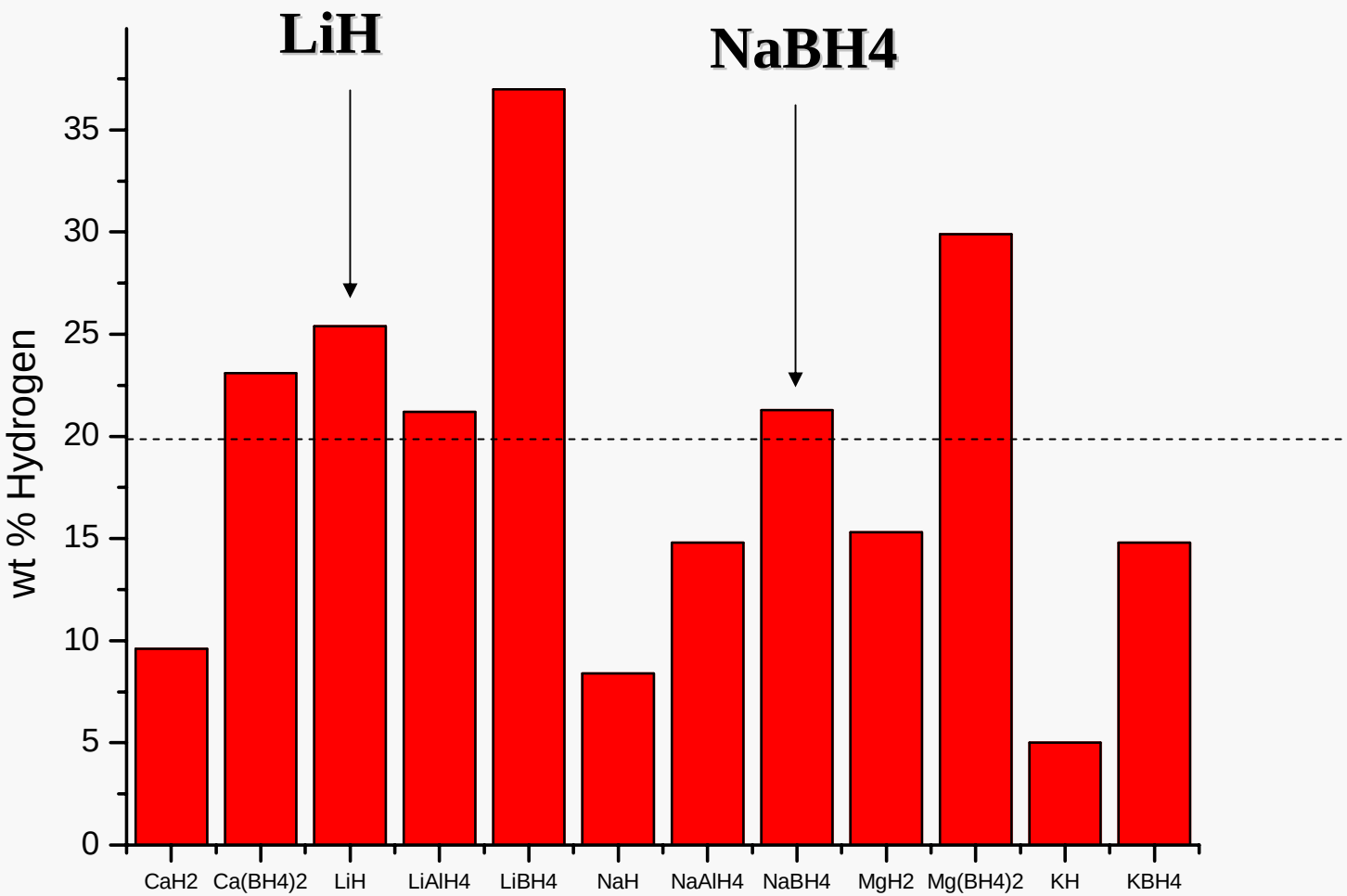
The hydrolysis of hydrides

- Reaction of some hydrides with water can represent an affordable method to produce hydrogen.

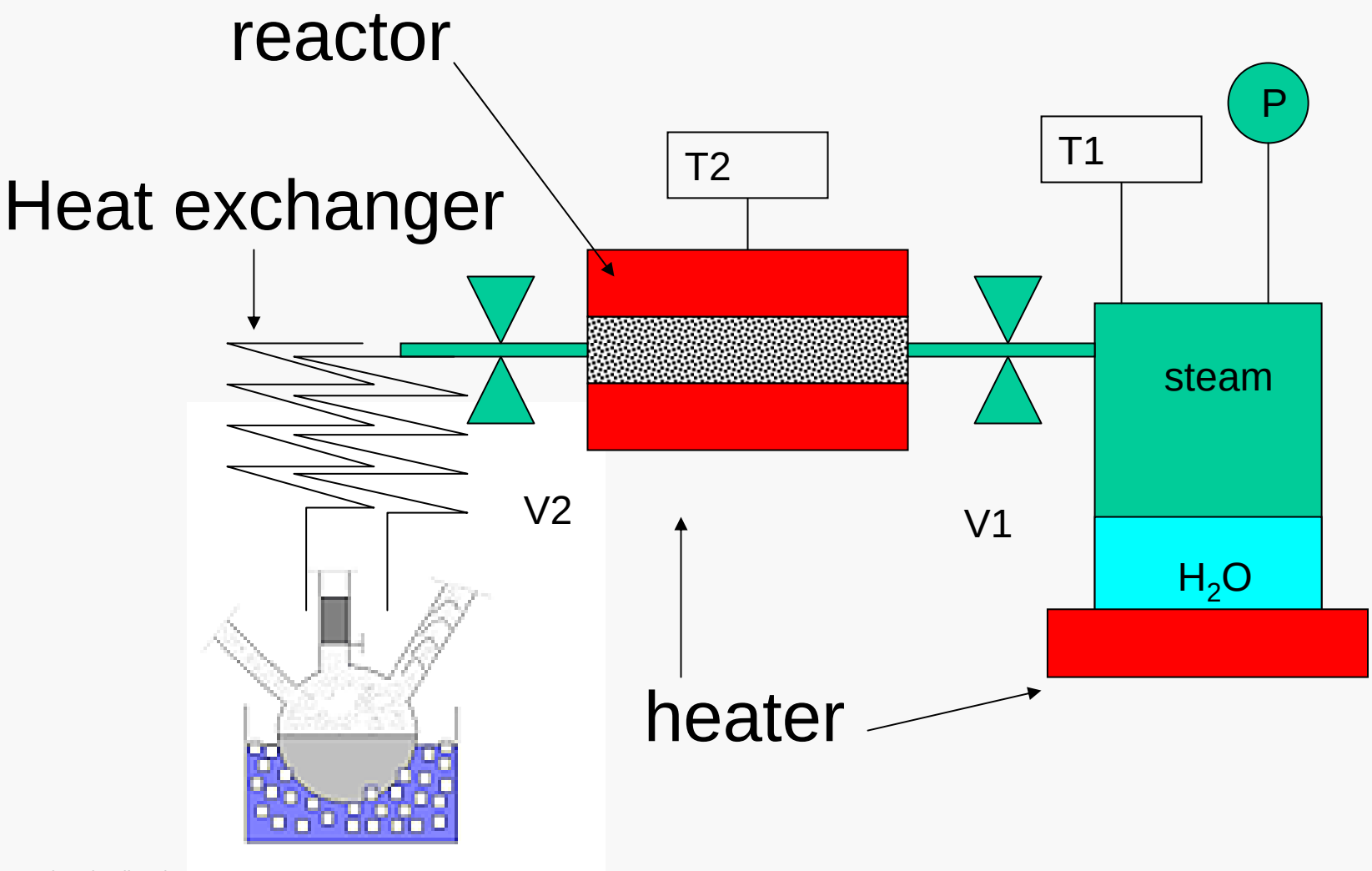
$$2\ MeH_n + n\ H_2O \rightarrow Me_2O + 2H_2$$

- The hydride must be regenerated off-board
- Considering fuel cell water recycling, the gravimetric energy density is very impressive!

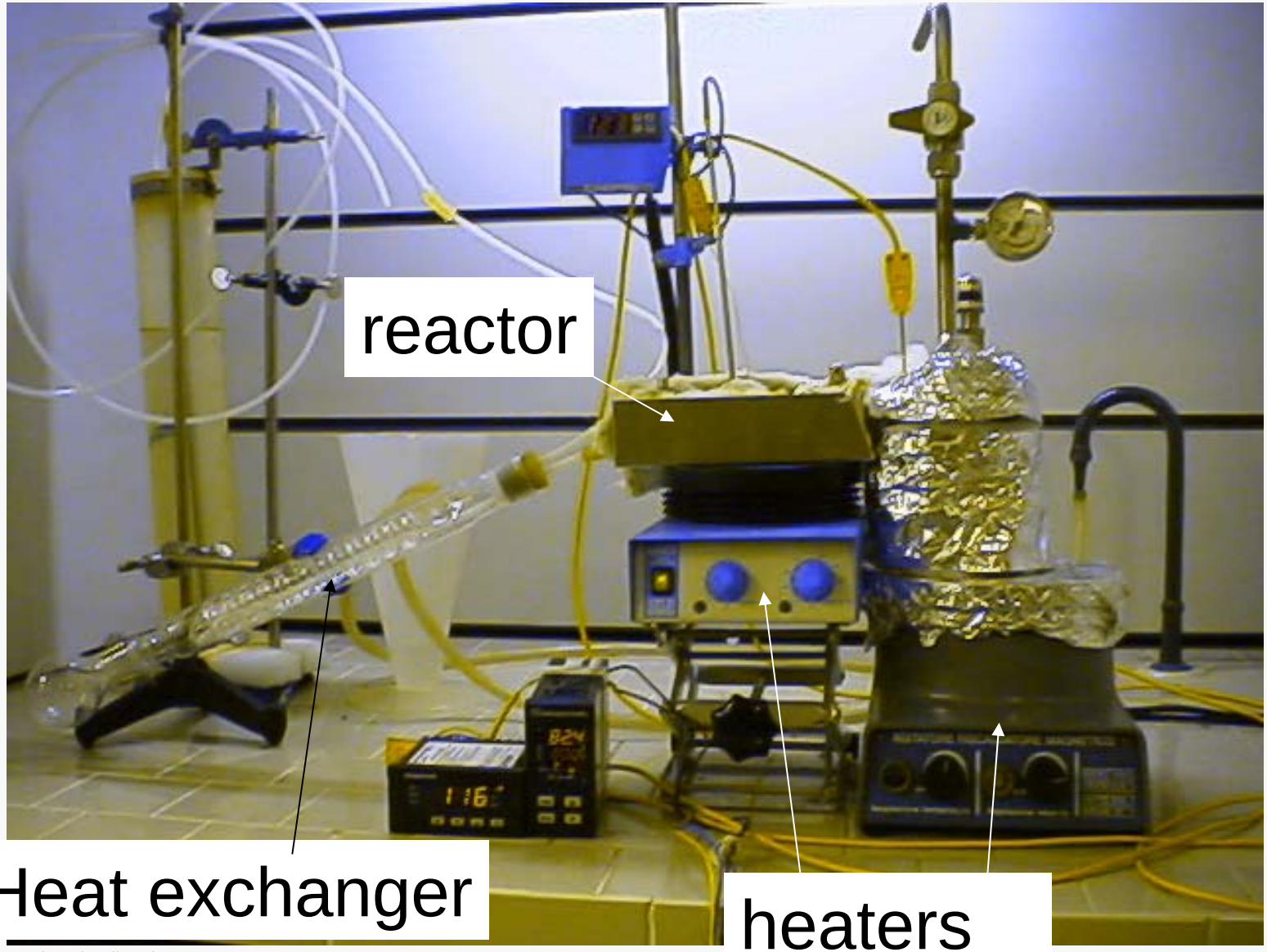
Among others, $NaBH_4$ and LiH have a theoretical hydrogen content higher than 20 wt. %



To test the steam hydrolysis of hydrides we set up the following apparatus



Set up for hydride hydrolysis



Results

- $NaBH_4$ is a very hygroscopic powder and tends to form a liquid phase when in contact with water vapor.
- The liquid phase (H_2O + $NaBH_4$) starts to produce hydrogen but the reaction is difficult to control due to the formation of foam.
- Sodium hydroxide, produced during the hydrolysis, prevents further hydrogen production.

$$NaBH_4 + 4H_2O \rightarrow NaOH + H_3BO_3 + 4H_2$$

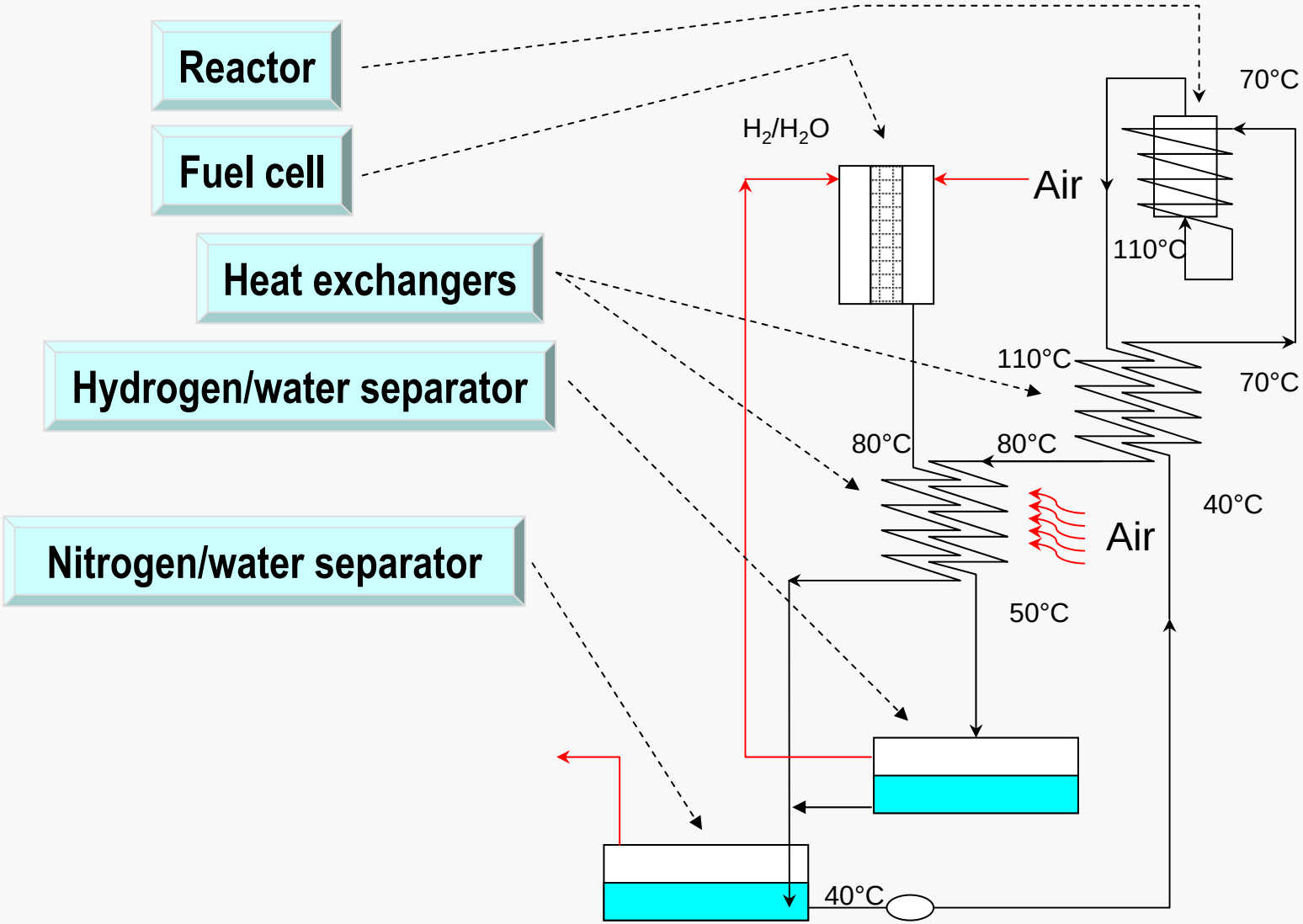
Hydrolysis of LiH

- The reaction products occupy a volume larger than the parent material thus occluding the reactor and causing system failure.
- The reaction enthalpy for hydrolysis is very high and heat management is required.

in addition:

- A mixture of hydrogen and steam is delivered at a temperature higher than the fuel cell working temperature.
- The mixture has to be cooled before getting to the fuel cell.
- The condensed water has to be recycled into the reactor.
- The exchanged heat has to be used to form steam

Schematic view of the complete system



The major problem is the cost

- LiH: the cost of lithium hydride is lower than the cost of metal lithium*.
- $NaBH_4$: about 60% of the cost is due to sodium metal. *

To reduce the cost both sodium production and hydride synthesis should be improved.

Not depending on the kind of metal hydride the cost is about 100 €/kg.

*Prices have been quoted for 0.5 kg batch.

“Got any money ?”

Na metal from molten NaOH

Reaction Medium	Molten NaCl	Molten NaOH
Operating Temperature	**600ºC**	**350ºC**
Anode Product	**Chlorine (Cl_2)**	**Water (H_2O)**
Theoretical voltage	**3.42 V**	**1.07 V**
Actual voltage	**~ 5.5 V**	**~1.2 V**
Separator	**Porous ceramic membrane**	**Selective sodium ion conducting ceramic membrane**

Ying Wu et al., Millennium Cell Inc., FY2004 Progress Report

Development of new $NaBH_4$ production process

$NaBH_4$ can be regenerated from borax using MgH_2

$$* \ Na_2B_4O_7 + 4MgH_2 \rightarrow 2NaBH_4 + 4MgO + B_2O_3$$

The use of other low cost reducing agent could decrease the $NaBH_4$ cost.

Magnesium = 20 €/kg

Aluminum = 15 €/kg

Carbon = very cheap

* **S. Suda et al.** Journal of Alloys and Compounds 349 (2003) 232–236

Solid metal hydride can meet some DOE requirements ….
……..but not all !

- To move toward a hydrogen-based economy some technological challenges have to be overcome.
- Parallel to technological improvements a new cultural model has to be developed.

“At the moment, only revisiting our style of life it will be possible to contribute to a cleaner environment.”