

<p>Issued by Air Liquide Laboratories Approved for distribution by Shigeyoshi NOZAWA</p> <p><b>Hydrogen supply by LiH hydrolysis, and LiOH recycle</b></p>	<p><b>Report:R2407</b> ----- <b>Date: September 21<sup>st</sup> 2007</b> ----- <b>Author:</b>  <b>Thomas Laude</b></p>
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## Table of contents

<b>SCOPE</b>	<b>3</b>
<b>SUMMARY</b>	<b>3</b>
<b>1. THE H<sub>2</sub> SUPPLY CONCEPT</b>	<b>4</b>
<b>2. CHEMICAL DENSITY</b>	<b>7</b>
2.1 PURE CHEMICAL DENSITIES	7
2.2 REAL DENSITIES	8
<b>3. SPECIFIC COSTS</b>	<b>10</b>
3.1 THE COST OF HYDROGEN AND METAL	10
3.2 ENERGY COST	11
<b>4. FEASIBILITY OF LIOH ELECTROLYSIS</b>	<b>12</b>
<b>5. KNOWN ACTIVITIES AND INTELLECTUAL PROPERTY</b>	<b>15</b>
5.1 LIOH RECYCLING	15
5.1 HYDROGEN SUPPLY	16
<b>6. ONE EXAMPLE OF APPLICATION: COUPLING WITH 350W AXANE SYSTEM</b>	<b>16</b>
<b>7. ACTIVITY MILESTONES</b>	<b>23</b>
<b>BIBLIOGRAPHY</b>	<b>24</b>

## Scope

This report follows a previous report entitled “*Hydrogen supply and energy storage through the reaction of light hydrides: Technical assessment*” (report R1106, March 2006). This report was screening a number of chemical solutions (including LiH) for hydrogen storage, mostly from thermo-physical properties.

Present report describes the LiH solution generally. More technical information about the electrolyser and the hydrolyser will be given in additional reports.

This report will also be completed by a market-oriented study, involving not only R&D but several marketing actors within the Air Liquide group and not limited to the LiH/LiOH cycle.

It is also parallel with a report on hydrogen supply on aluminium hydrolysis.

## Summary

Hydrogen can be supplied by lithium hydride hydrolysis:  $\text{LiH} + \text{H}_2\text{O} \Rightarrow \text{LiOH} + \text{H}_2$ . This is a hydrogen supply solution for fuel-cell customers, or for Industrial Merchant customers. It enables high hydrolyser density and high-power supply.

Dry solid LiH can also be used as a commodity for storage and distribution, where water is available at supply point. LiH has extremely high energy density, and hence enables savings on distribution, compared to high pressure solutions.

In terms, we expect this solution to be low cost, on the condition however that lithium metal is recycled. The heat loss cost during recycling should be negligible assuming recycling efficiency over 20%. Still, the feasibility of a LiOH electrolysis to Li is to be proven. One identified potential issue is the competitive formation of  $\text{Li}_2\text{O}$  during electrolysis.

Strategically, very few actors are openly active in the field. Key intellectual property could be secured, assuming successful LiOH electrolysis. An invention disclosure has been submitted (sub-0873) and is being processed by DSPI.

The business model for AL involves the management of a LiOH recycling station, which is important to remain a key player in the supply chain, but is also a difficulty for implementation of the distribution network. The station should consume hydrogen, however the relative consumption of  $\text{H}_2$  and electricity is still to be determined, as there are technical alternatives for the recycling.

All in all, lithium solution offers excellent performances, but still requires critical technical progress (LiOH electrolysis first, but also hydrolysis) and later, the implementation of a specific distribution network by AL.

We therefore believe that the LiH solution should be developed on a priority level, with a mid to long term perspective (6 to 10 years).

## Reminders

- Stable compounds of Li, O and H: Li, LiOH, Li<sub>2</sub>O, (Li<sub>2</sub>O<sub>2</sub>), O<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>
- Essential physical properties:

Li melting	180 C
LiH melting	689 C
LiOH melting	450 C
LiOH decomposition	924 C

## 1. The H<sub>2</sub> supply concept

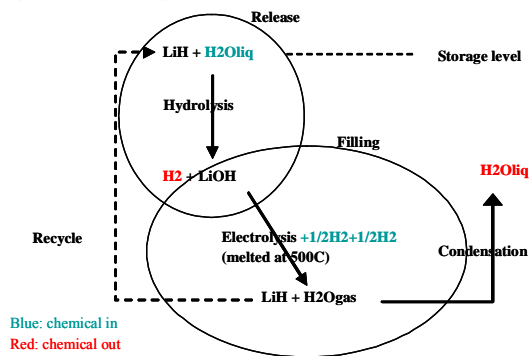
H<sub>2</sub> is supplied by the reaction:



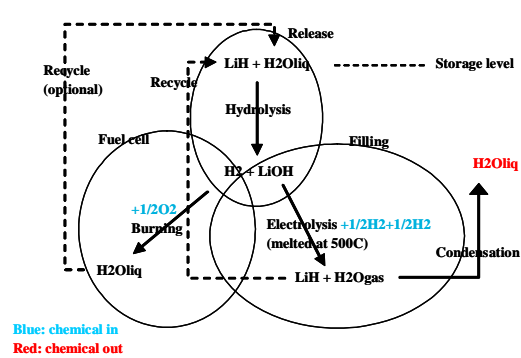
LiOH must be recycled because lithium is valuable. This is expected by melted electrolysis, ideally, with H<sub>2</sub> gas input. The Li electrolysis is a key demonstration that must be done for feasibility.

For a fuel cell user, water can also be returned from the fuel-cell during supply, to reduce system density.

HH cycle without water recycle



The HH cycle, including a fuel cell



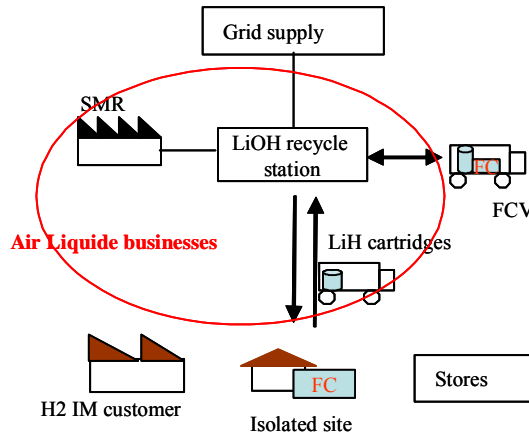
In a few words:

- Excellent storage density (including among other chemicals)
- No need to activate the hydrolysis
- LiOH should be recycled for cost validity

Such technique can be used either as a supply solution for a fuel-cell customer, or for an Industrial Merchant H<sub>2</sub> customer. Dry and sealed LiH can also be used as a fuel for storage and distribution.

Potential revenues for Air Liquide:

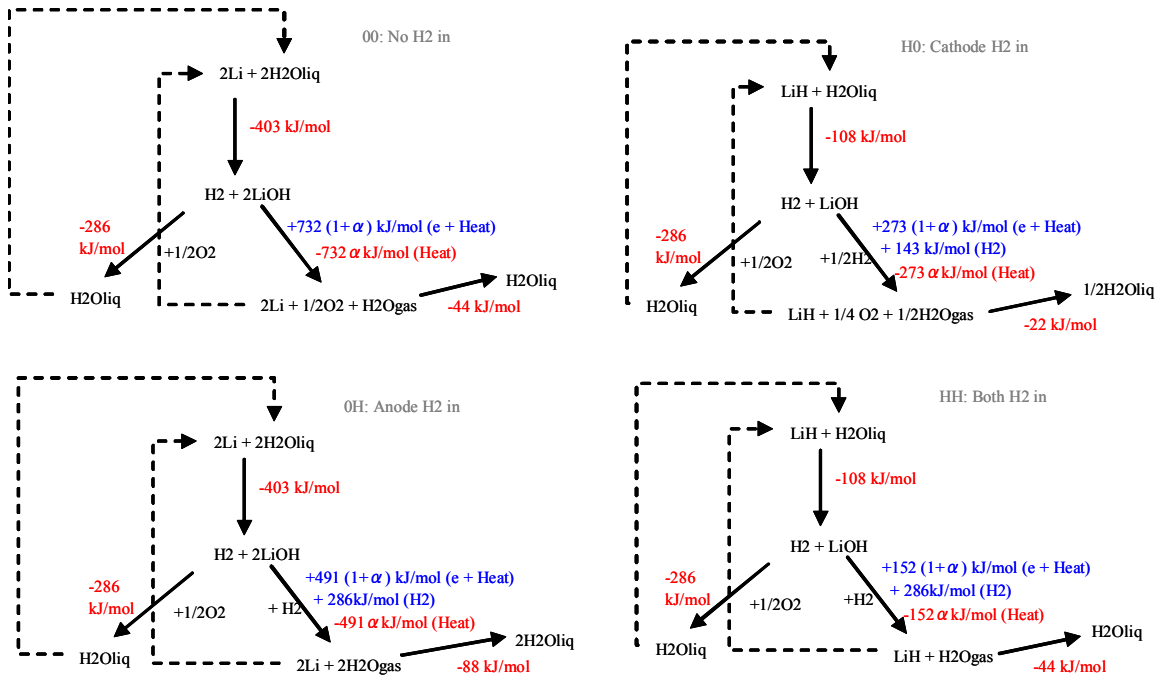
- Hydrogen sales for LiH recycling
- Hydrogen sales as LiH returnable cartridges, with cost reduction on distribution thanks to density
- New equipment and service sales



There are possible variations on the chemical cycle:

The 4 cycles

Blue: energy in  
Red: energy out



(Enthalpy values are for room temperature)

The two variations labelled OO and OH variations, based on Li metal, are not competitive supply solutions for density, heat efficiency, security and feasibility reasons. They are indicated only for reference.

The choice between HH and HO is yet opened, and will depend on performances and feasibility.

Recycling from LiOH to LiH would ideally be performed in a one step electrolysis. However it appears likely that, two steps will probably be necessary (electrolysis to Li, then hydrogenation.).

Heat losses can be estimated from the variations of enthalpy ( $\Delta H$ ) during each step of the cycle. Enthalpy is directly interpretable as the energy of the system. However, the efficiency of the recycling (electrolysis and hydrogenation) is unknown.

Detailed heat efficiency of the HH cycle		
<b>En. input (kJ/mol)</b>		
$A = 286 + 152(1 + \alpha)$		
<b>En. loss on input (kJ/mol)</b>	<b>En. Loss on output (kJ/mol)</b>	<b>Total energy loss</b>
$B = 44 + 152\alpha$	$C = 108$	$B + C = 152(1 + \alpha)$
<b>En. "Filled" (kJ/mol)</b>	<b>H2 En. output</b>	
$A - B = 286 + 152 - 44 = 394$	$A - B - C = 286$	
<b>input efficiency</b>	<b>output efficiency</b>	<b>Total efficiency</b>
$(A - B) / A = 394 / [286 + 152(1 + \alpha)]$	$(A - B - C) / (A - B) = 0.72$	$(A - B - C) / A = (1 + 152/286)(1 + \alpha)$
		<b>Non H2 En. in / H2 en. out ratio</b>
		$(B + C) / (A - B - C) = (152/286)(1 + \alpha)$

We note  $\alpha$  the corresponding ratio (heat loss / enthalpy step), so that recycling efficiency is  $1/(1 + \alpha)$ .

### Expected performances of the supply:

- High density of storage compared to other solutions (see dedicated chapter)
- Cost in an acceptable range, on the condition that LiOH can be recycled efficiently to LiH. (see dedicated chapter).
- Compatibility with high flow demand thanks to the high reactivity of the hydrolysis.
- Controllable output by controlling of water input of the hydrolyser.
- Customer is not submitted to high pressure regulation (pressure under 10 bar).
- Expected sufficient H2 purity for a fuel cell
- Acceptable for environment: Li compounds under air naturally turn to lithium carbonate (a well known medicine for the treatment of human depression). On the other hand, LiOH is corrosive, and a burning tank may release toxic fumes in vicinity.
- Mid security concerns: LiH is flammable in presence of water and air. This is common flammability (limited by oxygen supply) and not explosivity. In any case, a well sealed packaging is necessary as spontaneous ignition is possible.

## 2. Chemical density

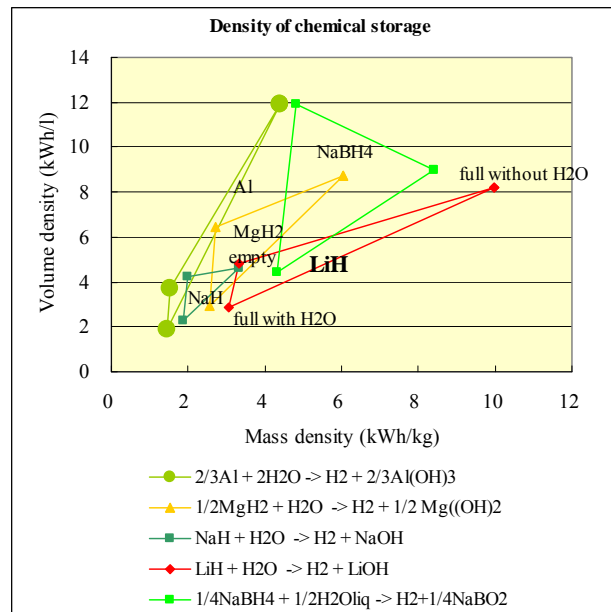
### 2.1 Pure chemical densities

The density of the pure chemical (no voids) is easily estimated.

		<b>LiH + H<sub>2</sub>O -&gt; H<sub>2</sub> + LiOH</b>		
		<b>Full</b>		<b>Empty</b>
		<b>No water</b>	<b>With water</b>	
	<b>Compared</b>	H <sub>2</sub> /(LiH)	H <sub>2</sub> /(LiH+H <sub>2</sub> O)	H <sub>2</sub> /(LiOH)
<b>Mass density</b>	<b>kg of H<sub>2</sub>/kg</b>	25.36%	7.76%	8.42%
	<b>kWh/kg</b>	9.988	3.058	3.315
	<b>MJ/kg</b>	35.958	11.009	11.935
<b>Volume density</b>	<b>kg of H<sub>2</sub>/l</b>	0.207947766	0.072748978	0.1228926
	<b>kWh/l</b>	8.191	2.865	4.840
	<b>MJ/l</b>	29.486	10.315	17.426
<b>Dimensions</b>	<b>kg/kg of H<sub>2</sub></b>	3.943	12.880	11.880
	<b>l/kg of H<sub>2</sub> (no void)</b>	4.809	13.746	8.137

This density is different if water is included or not in the estimation, and this depends on water availability for a given application. Also, oxygen is progressively trapped into the tank as reaction proceeds. We can consider a emptied density (total H<sub>2</sub> supplied/final chemical mass or volume).

Hence, pure chemical density can be described as 3 points:



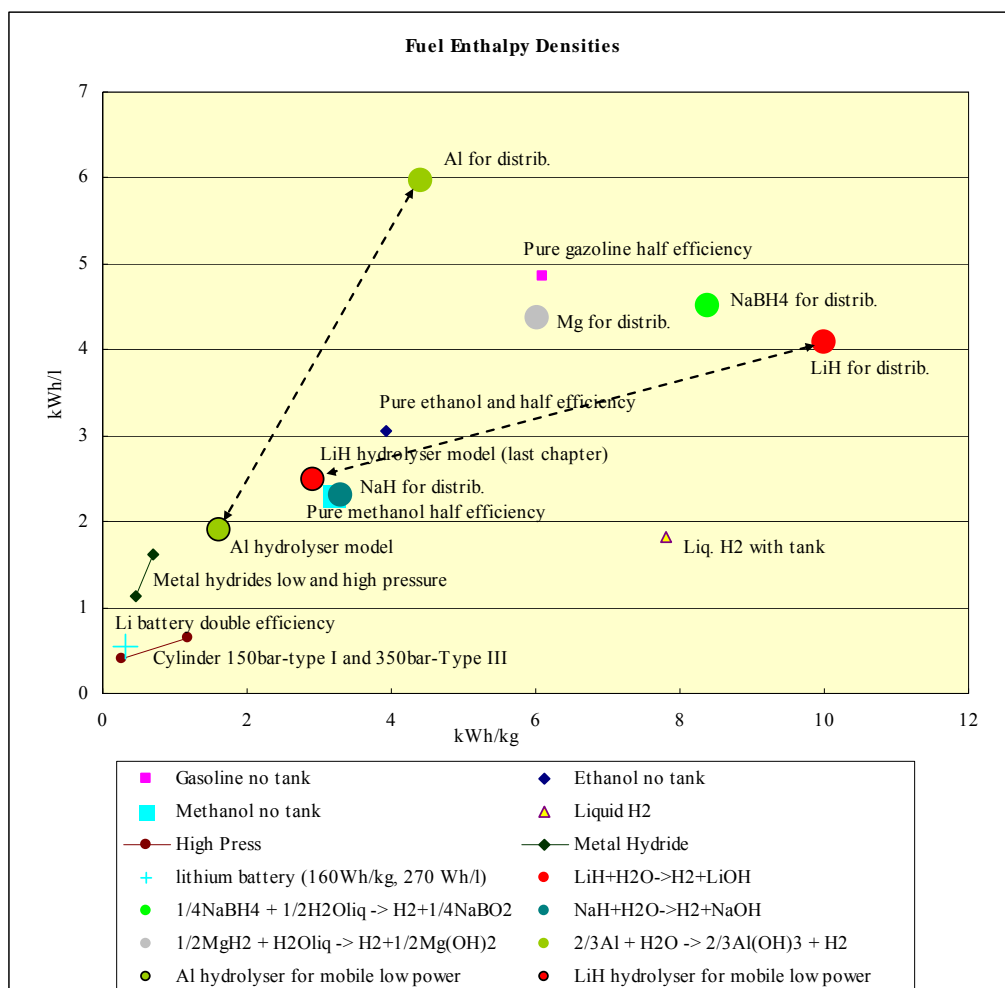
If comparing pure chemical density, LiH is excellent among other chemical solutions for mass density, with a remarkable density if water is not carried (dry fuel density).

However this simple comparison is not conclusive as each chemical is affected differently by other factors in the practical application as a H<sub>2</sub> storage media.

Mass density Comparison of the 4 cycles

Cycle	Full				Empty	
	No water		With water			
<b>0</b>	H <sub>2</sub> /(2Li+H <sub>2</sub> O) =	6.32%	H <sub>2</sub> /(2Li+2H <sub>2</sub> O)	4.04%	H <sub>2</sub> /(2LiOH) =	4.21%
<b>0H</b>	H <sub>2</sub> /(2Li+H <sub>2</sub> O) =	6.32%	H <sub>2</sub> /(2Li+2H <sub>2</sub> O)	4.04%	H <sub>2</sub> /(2LiOH) =	4.21%
<b>H0</b>	H <sub>2</sub> /LiH =	25.36%	H <sub>2</sub> /(LiH+H <sub>2</sub> O)	7.76%	H <sub>2</sub> /(LiOH) =	8.42%
<b>HH</b>	H <sub>2</sub> /LiH =	25.36%	H <sub>2</sub> /(LiH+H <sub>2</sub> O)	7.76%	H <sub>2</sub> /(LiOH) =	8.42%

## 2.2 Real densities



Hypotheses:

- For chemical distribution, mass density is that of chemical (no water carried), and volume density is that of the chemical divided by a factor 2 to account for powder voids and packaging.
- Aluminium hydrolyser density is based on case-study for mobile low-power application (see [4.4.1] )
- LiH hydrolyser density is based on case-study for mobile low-power application (last chapter)
- For liquid hydrocarbon, density does not include tank and liquid densities ([http://xtronics.com/reference/energy\\_density.htm](http://xtronics.com/reference/energy_density.htm)) are divided by a factor 2 to take into account the low efficiency of combustion engines compared to H<sub>2</sub> fuel cells.
- For lithium battery (ref [http://en.wikipedia.org/wiki/Lithium\\_ion\\_battery](http://en.wikipedia.org/wiki/Lithium_ion_battery)) density are doubled to account for the fact that electricity can be



converted efficiently to useful energy.

- Cylinder type I is 15kg, 10 litter (as used in ALL), Cylinder type III is as reported in Toyota report (mater res soc symp proc 884E 2005): 350bar, 3kg H<sub>2</sub>, 100kg, 180l
- Metal hydride is based on the same Toyota report: low pressure MH (3.5kg H<sub>2</sub>, 300kg, 120l, 10bar); and high presure MH (7.3kg H<sub>2</sub>, 420kg, 180l, 350bar)
- Liquid H<sub>2</sub> is assumed 20%H<sub>2</sub>mass, and +30%nonH<sub>2</sub> of tank volume

Real chemical storage density is complex to describe, because it depends on the application. Globally we may distinguish between density for distribution and density for supply.

Density for distribution is the fuel density when transporting to the customer. In above graph, we considered that the density for distribution is that of the dry chemical powder, hence that of the dry chemical with 50% volume lost in voids. Chemical density is high for any chemical. LiH is remarkable for mass density.

Density for distribution is very important to reduce distribution costs, and hence we can expect savings on distribution.

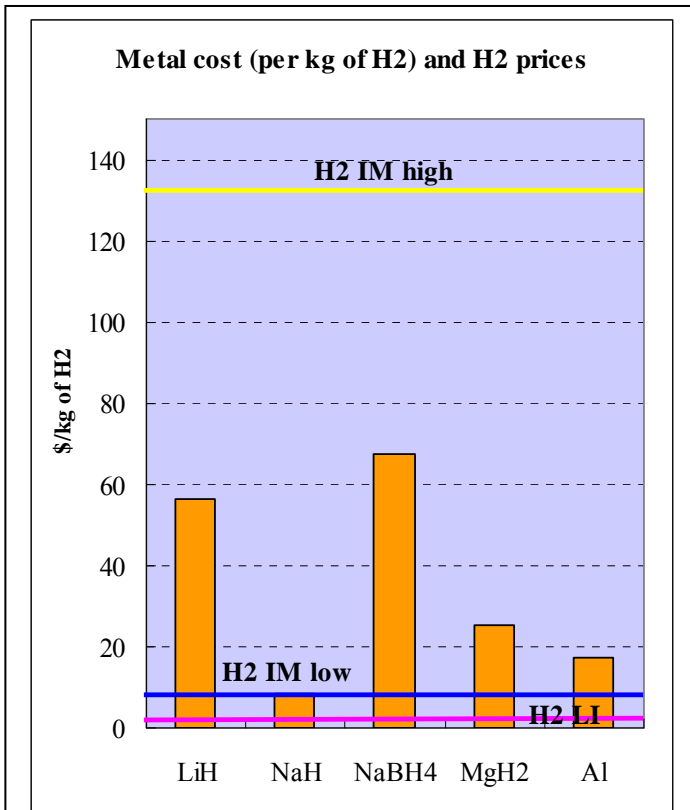
Density of the supply is the density of the full supply system (hydrolyser). High density of the supply is essential for some application, especially mobile applications such as small vehicles or portable fuel cells.

Density of the supply is more complex to estimate, and requires a modelisation for each application (see case study of last chapter). We have to take into account that:

1. Water may be included fully, partially, or not at all in the estimation. This depends on water availability for the user:
  - For stationary applications where water is available from the tap, water does not need to be taken into account.
  - For fuel cell users, a (partial) recycle of water from the fuel cell is possible.
  - For other applications, full water should be taken into account.
2. The mass of the supply increase with usage, as oxygen is progressively trapped into the tank. It should be considered how often the waste chemical is discarded or collected.
3. Some chemical form hydrates in the waste chemical trapping water and hence reducing density. This is especially the case of NaBH<sub>4</sub> [NaBO<sub>2</sub>.(H<sub>2</sub>O)<sub>3</sub> hydrate], and LiH [LiOH.H<sub>2</sub>O hydrate] (LiOH.H<sub>2</sub>O dries between 100C and 150C at 1 bar).
4. Some hydrolysers require several chambers, which severely increases hydrolyser volume. This is especially true for NaBH<sub>4</sub>, as it is catalytic.
5. The reaction in usually incomplete.

### 3. Specific costs

#### 3.1 The cost of hydrogen and metal



Chemical cost. We had to use severe approximations:

- For common metals like Al or Mg, market is large, and hence metal price are available and relevant. (hydrogenation cost is neglected)
- For lithium, metal prices are not relevant because market is very small. However, treatment cost being negligible to lithium intrinsic chemical cost, any large-scale compound is relevant (we use LiOH.H<sub>2</sub>O cost)
- For sodium, metal market is small, and intrinsic chemical cost is low (NaCl is virtually free). Prices are mostly treatment-driven. We use NaOH cost, which is the chemically closest large-scale compound. This is probably a poor underestimation
- For NaBH<sub>4</sub>, minimal future cost has been estimated in a different AL study (conversion, 1 eur = 1.2 \$).

Element	\$/kg
Li as LiOH.H <sub>2</sub> O	14.3
Li as LiCO <sub>3</sub>	14.0
Na as NaCO <sub>3</sub>	0.397
Na as NaOH	0.696
Na as Na <sub>2</sub> SO <sub>4</sub>	0.456
Na as NaCl	0.0178
Mg as MgO	0.663
Mg as Mg(OH) <sub>3</sub>	2.115965903
Mg as MgCl <sub>2</sub>	1.101123209
Mg as Mg	3.858E+00
Be as Be(OH) <sub>2</sub>	54.04405306
Be as Be	1.400E+02
Al as Al <sub>2</sub> O <sub>3</sub>	0.700982777
Al as Al	1.940E+00
B as Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> .5H <sub>2</sub> O	2.695E+00
NaBH <sub>4</sub> present	40 eur/kg
NaBH <sub>4</sub> minimal future	12 eur/kg

Source: US geological survey, except NaBH<sub>4</sub> (AL internal study of B. Orsal)

Recycling metal is a necessity for the LiH solution. Indeed, if we compare hydrogen prices to the metal cost of the LiH solution without recycling (56\$/kg of H<sub>2</sub>), it is clear that lithium cost would add a heavy burden on hydrogen price, for most markets.

For hydrogen, we assumed the following prices: (from AL 2006 AII report with conversion 1 eur = 1.2 \$)

- Large Industry ~ 2.7 \$/kg, (0.24 \$/Nm<sup>3</sup>)
- Industrial Marchand: 8.7 to 133 \$/kg (0.78 to 12 \$/Nm<sup>3</sup>)

### 3.2 Energy cost

Energy is output as H<sub>2</sub>, however it is input both as H<sub>2</sub> and electricity. Hence energy cost depends not only on heat losses, but also on the relative prices of H<sub>2</sub> and electricity:

**Price H<sub>2</sub> out = (H<sub>2</sub> energy in / H<sub>2</sub> energy out).Price of H<sub>2</sub> energy in**  
**+ (electrical energy in/ H<sub>2</sub> energy out).Price of electrical energy in**

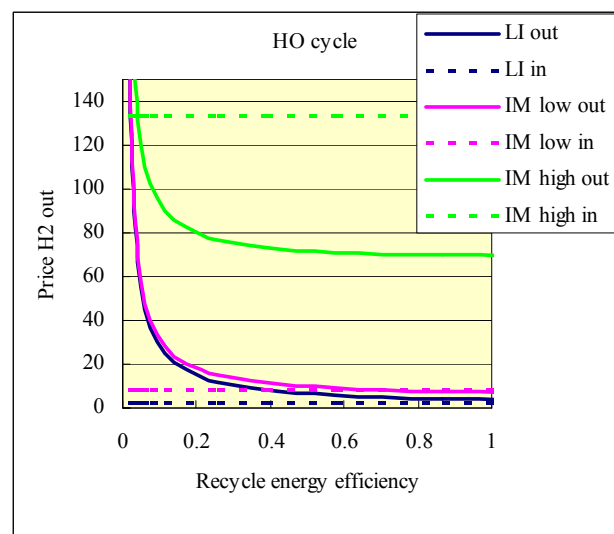
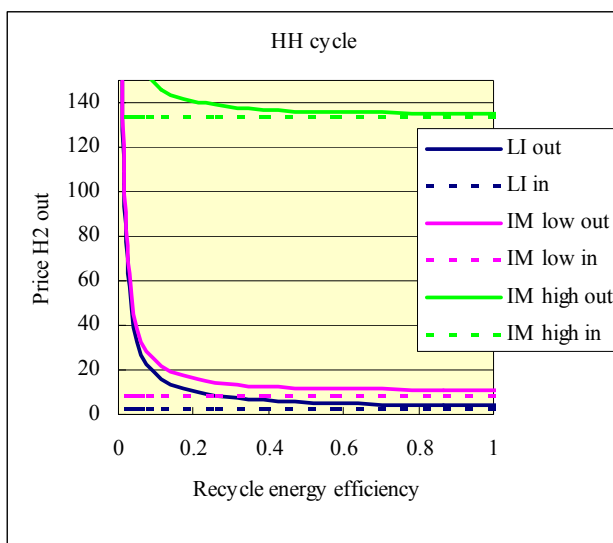
It should be noted that the price of H<sub>2</sub> input in is far more local than the price of electricity. The price of H<sub>2</sub> input depends on where LiOH is recycled within the H<sub>2</sub> distribution network: close to a SMR unit, close to the customer, ... It also varies with countries. On the other hand electrical prices are rather uniform, assuming, a connection to the grid.

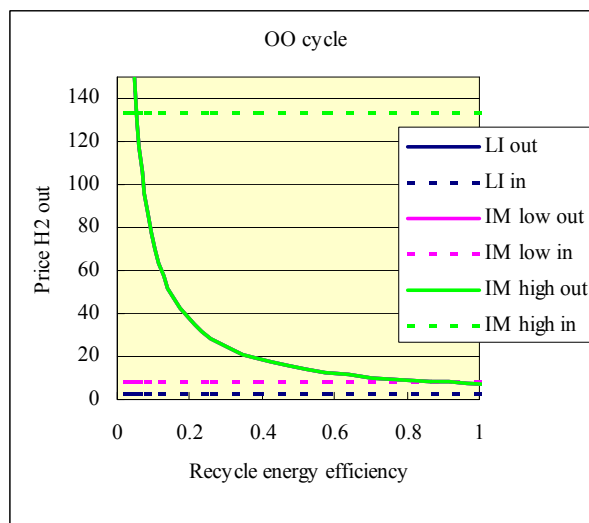
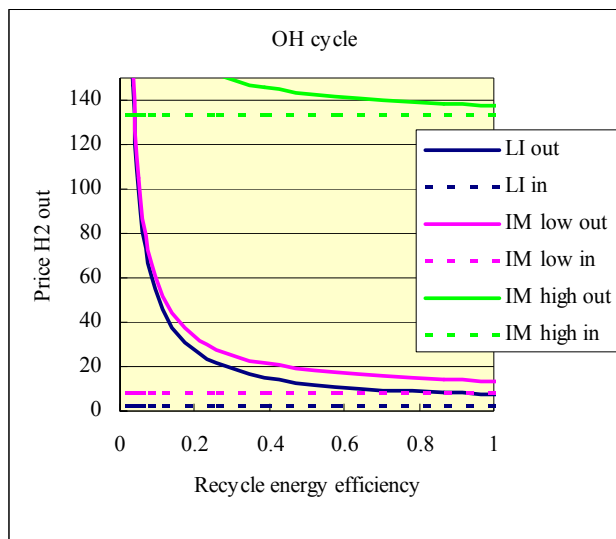
The table and graphs below indicates H<sub>2</sub> price out for the four cycles presented earlier (see enthalpy figure of chapter 1),

Comparison	H <sub>2</sub> price out
<b>00</b>	$[(732/286)(1+\alpha)Pel]$
<b>0H</b>	$[Phyd + (491/286)(1+\alpha)Pel]$
<b>H0</b>	$[Phyd/2 + (273/286)(1+\alpha)Pel]$
<b>HH</b>	$[Phyd + (152/286)(1+\alpha)Pel]$

Phyd = price of H<sub>2</sub> input, Pel = price of electrical input,  $\alpha$  = recycling heat loss/ recycling enthalpy step

For the graphs below, we assume Pel = 0.06 eur/kWh (~2.84 \$/kg of H<sub>2</sub>)





For OO cycle, the three traces are superposed

Graphs above give the following information:

- Energy cost is not linear with recycle efficiency. Instead, it flattens above a given efficiency. For instance, efficiency over 20% is sufficient for HH and HO cycles. The reason is mostly that heat losses are paid with cheap electrical energy rather than hydrogen. For reference, NaOH electrolysis with a 1930 Castner-Tiegel electrolyser, may reach about 50% efficiency with H<sub>2</sub> recycling.
- If H<sub>2</sub> in price is high (IM high), replacing hydrogen input by electrical input can reduce cost drastically (considering an acceptable recycling efficiency): For OO (no H<sub>2</sub> is input), H<sub>2</sub> output price is that of electricity. For HO (1/2 H<sub>2</sub> in), H<sub>2</sub> price out is about half of H<sub>2</sub> price in. For HH and OH (1 H<sub>2</sub> in), H<sub>2</sub> output price is about same as H<sub>2</sub> input price in.
- Where H<sub>2</sub> in price is low (LI), H<sub>2</sub> out price may be notably higher than H<sub>2</sub> in. However, it is not an issue, as such cost is small compared to further distribution cost.

If we assume that distribution (including recollection) cost of solid lithium is notably cheaper than the distribution of H<sub>2</sub> gas, but notably more expensive than heat losses, then:

- It is best to recycle near H<sub>2</sub> production site (to replace gas distribution by solid lithium distribution)
- The final price of the solution will mostly depend on distribution cost
- The final price of the solution will be lower than that of traditional high pressure solutions

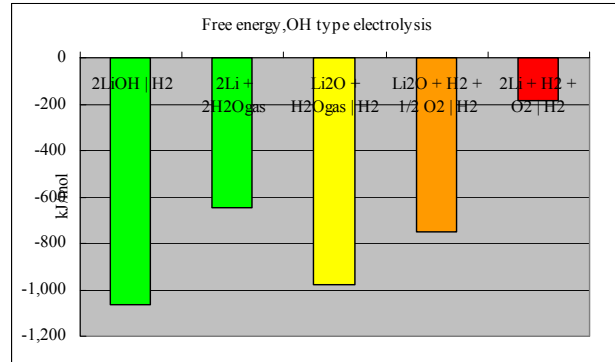
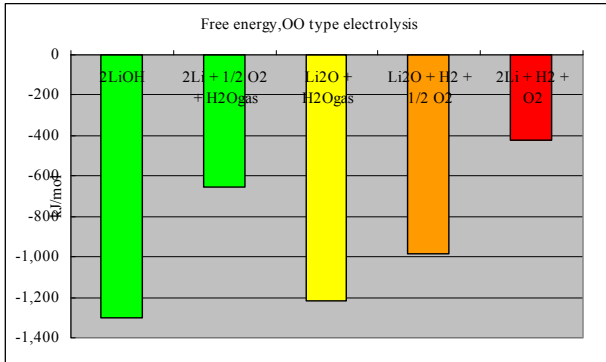
#### 4. Feasibility of LiOH electrolysis

In term of feasibility, all steps of the cycle are known from previous art, except the electrolysis of

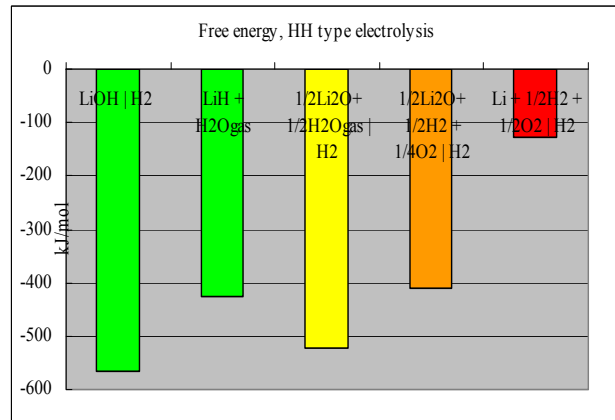
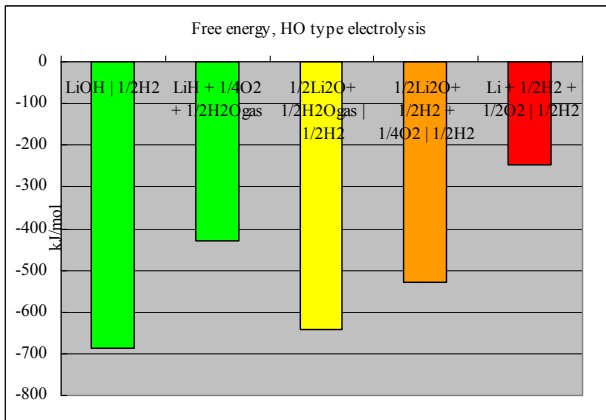
LiOH to Li or LiH. It is therefore the first object of R&D efforts.

On the other hand, electrolysis of NaOH to Na, which is a very similar compound, is known.

As one example of the potential difficulties of the electrolysis, the figures below illustrates free energies: before electrolysis, after electrolysis (in green), and some possible side reactions (yellow, orange and red). We consider the 4 possibilities of hydrogen inputs on electrodes.



(We indicate by “|” physical separations of the compound at the end of the step.)



The water forming reaction  $2\text{LiOH} \Rightarrow \text{Li}_2\text{O} + \text{H}_2\text{O}$  (yellow) is not expected electrolytic. Although it is competitive for free energy, and indeed is known to exist spontaneously, around melting (450C) at low water vapour pressure [3.5.2], it does not seem separable in redox reactions at electrodes.

The decomposition to the elements  $\text{LiOH} \Rightarrow \text{Li} + 1/2\text{O}_2 + 1/2\text{H}_2$  (red) is not expected problematic. This is separable into:  $\text{LiOH} \Rightarrow \text{Li}^+ + \text{H}^+ + 1/2\text{O}_2 + 2e$  at anode, and  $\text{Li}^+ + \text{H}^+ + 2e \Rightarrow \text{Li} + 1/2\text{H}_2$  at cathode, however it would require too much energy to be competitive (unless voltage is overset).

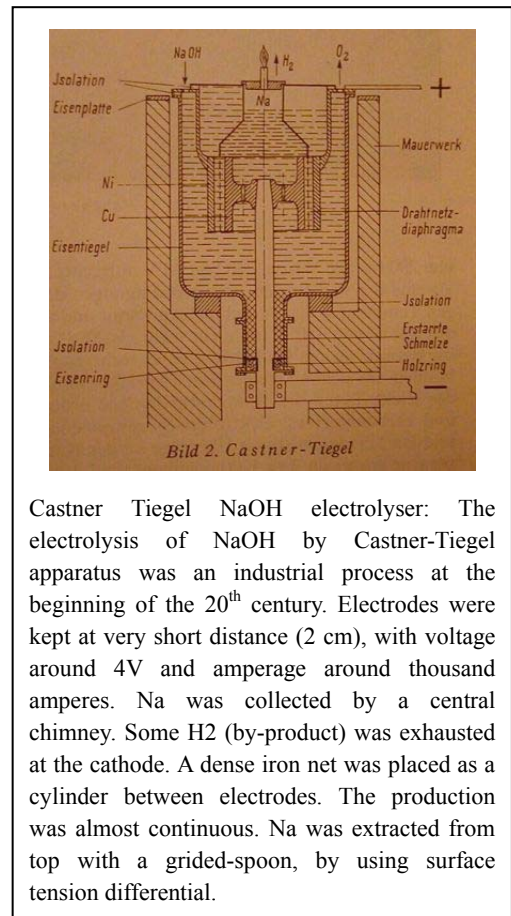
On the other hand, the reaction:  $2\text{LiOH} \Rightarrow \text{Li}_2\text{O} + 2\text{H}_2 + 1/2\text{O}_2$  (orange) is cumbersome. It is energetically competitive and it can be separated into:  $2\text{LiOH} \Rightarrow \text{Li}_2\text{O} + 2\text{H}^+ + 2e + 1/2\text{O}_2$  at anode, and  $2\text{H}^+ + 2e \Rightarrow \text{H}_2$  at cathode.

Such reaction would be detected by the formation of  $\text{H}_2$  at cathode. And indeed, the by-production of  $\text{H}_2$  at cathode during  $\text{NaOH}$  electrolysis by Castner-Tiegel electrolysis is well known.

Considering this, it is almost surprising that a Castner Tiegel electrolysis can produce sodium metal at all. We could expect the continuous precipitation of solid  $\text{Na}_2\text{O}$  below the anode. This is not the case however.

Present hypothesis is that the solubility of  $\text{Na}_2\text{O}$  in molten  $\text{NaOH}$  is relatively high, and thanks to that,  $\text{Na}_2\text{O}$  can migrate to cathode and later decompose, producing sodium metal.

It should be determined if the same mechanism is possible for  $\text{LiOH}$  electrolysis.



Castner Tiegel NaOH electrolyser: The electrolysis of  $\text{NaOH}$  by Castner-Tiegel apparatus was an industrial process at the beginning of the 20<sup>th</sup> century. Electrodes were kept at very short distance (2 cm), with voltage around 4V and amperage around thousand amperes.  $\text{Na}$  was collected by a central chimney. Some  $\text{H}_2$  (by-product) was exhausted at the cathode. A dense iron net was placed as a cylinder between electrodes. The production was almost continuous.  $\text{Na}$  was extracted from top with a grided-spoon, by using surface tension differential.

## 5. Known activities and intellectual property

### 5.1 LiOH recycling

Lithium metal is traditionally produced by the electrolysis of LiCl. This has proven the most cost efficient way to produce lithium from available lithium carbonate. [3.2.1, 3.2.2, 2.1.1]

The electrolysis of melted LiOH to Li (or to LiH) is not reported today. It is therefore both a challenge and a chance to secure intellectual property.

On the other hand, Li<sub>2</sub>O is simply obtained by LiOH dehydration (over melting point). Then, electrolysis of Li<sub>2</sub>O is possible at high temperature. It was reported with carbonate-fluoride eutectic mixture at 750-900C, with carbon reactor, carbon anode and melted tin cathode. [2.1.2]

Production of lithium by aqueous LiOH electrolysis is also known. However this technique use cumbersome mercury amalgam. [2.1.3, 2.1.4]

The electrolysis of NaOH to Na (“Castner-Tiegel” electrolyser), which is very similar in principle to LiOH, is well known. It was the industrial technique to produce sodium metal before being replaced by NaCl electrolysis around 1930 [3.9.3]. It was replaced for the following reasons:

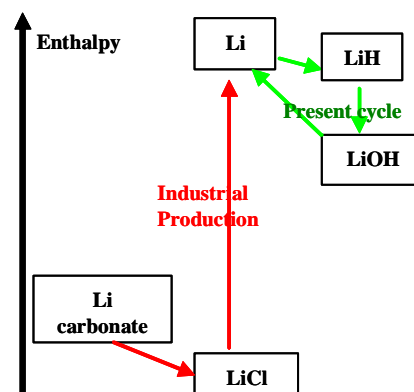
- Higher efficiency (NaOH electrolysis efficiency was limited by unused by-product H<sub>2</sub>)
- NaCl is virtually free
- Economical interest of reselling by-product chlorine gas

Note that these reasons do not apply to the present need of LiOH recycling.

Millenium cell & Air products, although not involved in lithium electrolysis, have developed the technique of electrolysing NaOH while H<sub>2</sub> is input at anode. This technique is equivalent to replacing part of the electrical input by an H<sub>2</sub> input. It is favourable for efficiency and corrosion reduction at anode, however it may be difficult to industrialise because of three phase reaction. Also it may not be economically viable, as the cost of H<sub>2</sub> input is usually higher than that of electricity.

Lately, Millenium cell & Air products have focused on direct electrolysis from borates. Indeed they aim at NaBO<sub>2</sub> recycling for NaBH<sub>4</sub> supply solutions. [2.1.5, 2.1.6, 3.9.1, 3.9.2]

Several carbo-reduction of LiOH to Li are also possible theoretically. However, efficiency is of



concern. [2.2.1, 2.2.2, 3.6.2]

## 5.1 Hydrogen supply

Hydrolysis of LiH to produce hydrogen is a long known technique. The reaction is therefore IP free. [3.5.1]

However some techniques related to packaging, or to the hydrolyser are patent pending. [2.4.1, 2.4.2, 2.4.4, 2.5.1, 2.5.2] None seems critical.

Safe hydrogen LLC have been particularly visible in the technique of LiH packaging in oil slurry. [3.6]

## 6. One example of application: Coupling with 350W Axane system

The following example is given for comparison with aluminium hydrolyser model [4.4.1].

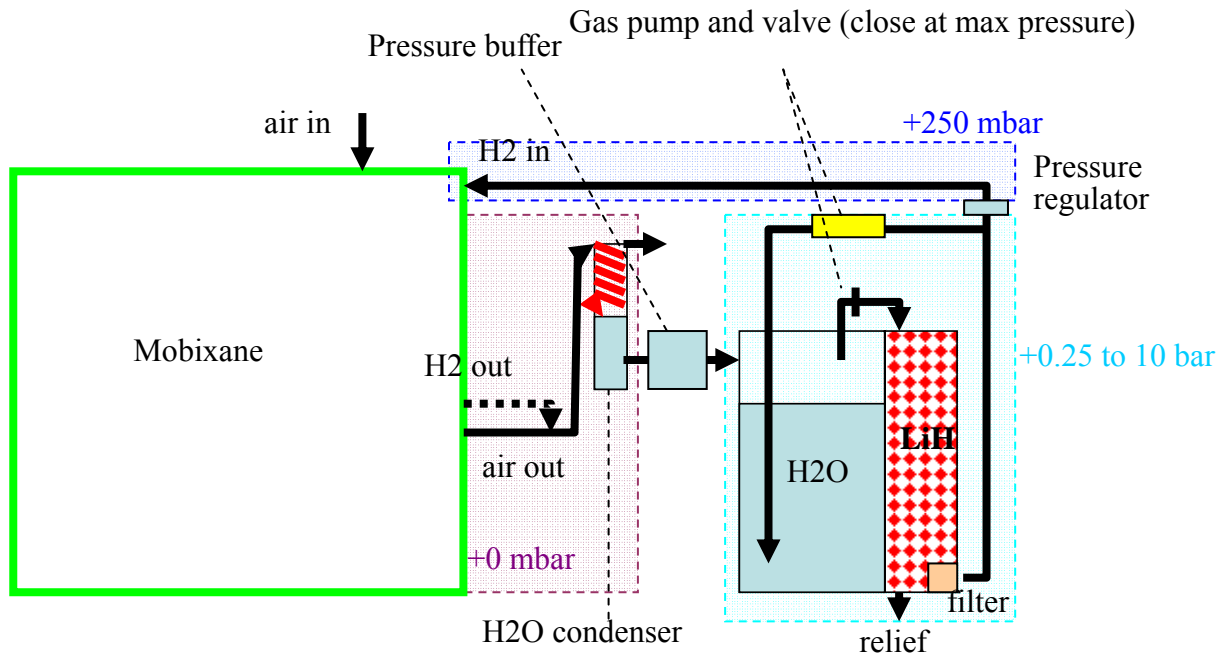
### Need

We need a storage/supply system to be coupled with a low-power/mobile generation system. Today, such system is being developed by Axane for wheelchair as a delivery of Hychain program, but will evolve to different applications in the future. Axane system supplies 350W electrical output, for about 20 l and 15 kg. It uses 16 cells and no humidifier.

### Main technical expectations for the H<sub>2</sub> supply:

- H<sub>2</sub> purity compatible with a fuel cell
- Constant pressure +250mbar on FC input
- Stable flow between 0 and 0.35 Nm<sup>3</sup>/h (about 0 to 0.35 kW considering 40% FC efficiency)
- Transient flows on FC input up to 1 Nm<sup>3</sup>/h
- Stabilisation time compatible with the FC (3.5s for start up)
- Massic and volumic density superior to cylinder type I solutions
- Volume around 10 l
- Ease of use and security





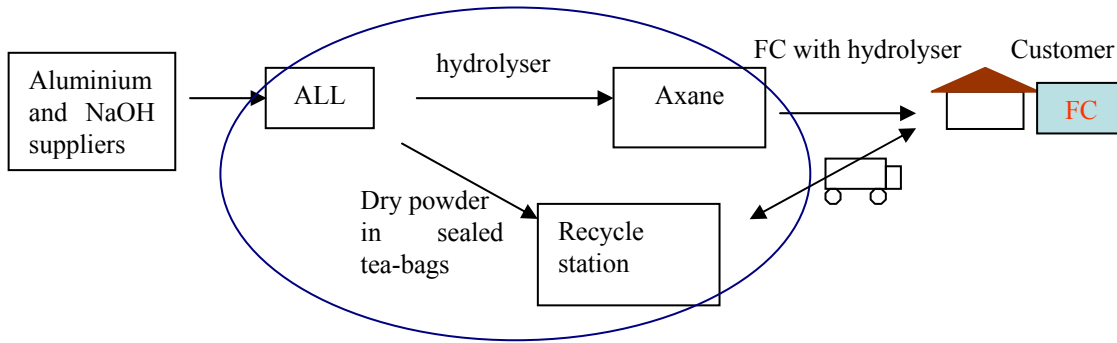
### Technical Solution

- Powder is dry LiH.
- Powder is packaged collectable cartridges (“tea-bag” type) under a sealed packaging (to protect from air).
- Only one cartridge is used at a time, but customer has a number of cartridges in stock.
- Water is input on the powder as vapor, but may also be input as liquid for faster input. To control water input, and hence pressure inside the tank, we use an automatic H<sub>2</sub> recirculation system that closes over a given pressure.
- Water input is from tank top to maximize reacted powder. Cross section of the cartridge is adapted to output flow.
- H<sub>2</sub> is output from tank bottom to output dry gas. It is equipped with particle filter.
- Hydrolyser output is connected to FC H<sub>2</sub> input. Pressure is regulated below +250mb to avoid overpressure on the PEM
- A limited pressure is built in the storage tank. This allows transient fluctuations of the output flow. However pressure is kept below high pressure levels (10bar) for usability and tank limited strength. Relief valve is present for security.
- Water is collected on FC output with a condenser.
- Cycled water is looped back to the storage using a pressure buffer.

### Business model

- Hydrolyser system is provided by AL with the fuel-cell system
- Powder cartridges are supplied to the customer by AL

#### Business model at development stage



## Expected Technical performance

For the following, we consider that the user carries 5 cartridges of 1kg each in addition to the hydrolyser.

### 1. Storage density

Modelization is based on the followings hypotheses:

FC water recycling rate	0.8	
reaction complet rate	0.7	Stoichiome
number of cartridge	5	
mass 1 one cartridge	1	kg
System mass	2	kg
Min available H2 volume	1	l
Set pressure for water stop	4	bar
Non-tank volumes	1	l
Powder volume ratio	0.6	
FC efficiency	0.4	

Cylinder type I for comparison	
mass	15 kg
pressure	150 bar
volume	10 l
H2 density	9.1612 kg/m3

Reaction completion ration is supposed relatively low (70%) to account for the formation of LiOH.H2O hydrate.

### Autonomy

Autonomy	kg H2	Nm3	kWh FC out
1 cartridge	0.17752	2.697817	2.7967676
Total cartridges	0.88758	13.48909	13.983838

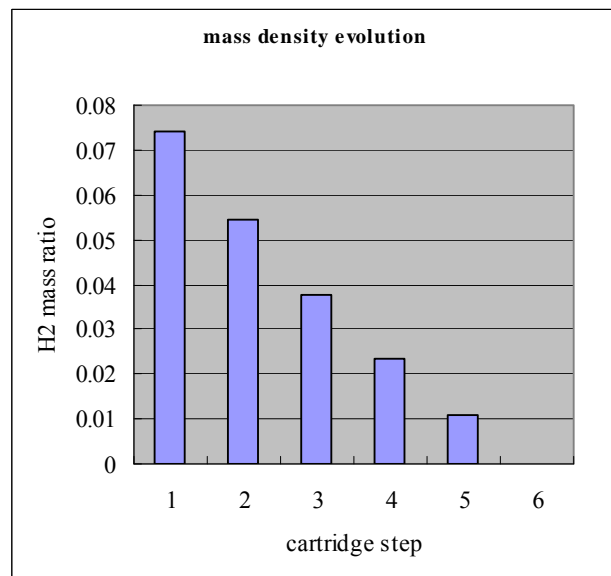
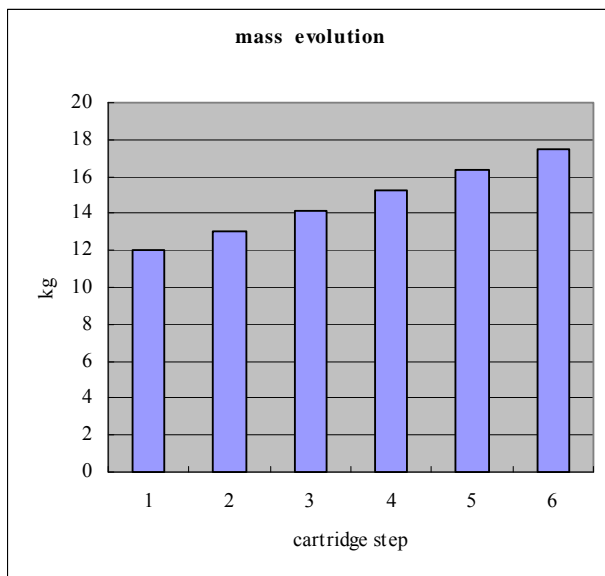
Comparison to Cylinder type I			
Autonomy	kg H2	Nm3	kWh FC out
	0.09161	1.39228	1.443345481

The H2 content of the storage (with 5 cartridges) is about 10 times that of a 10-liter type-I cylinder (which has comparable mass and volume. See below.).

At full power (350W), the autonomy (with 5 cartridges) is 40 hours. This is enough for a day to day usage. In addition, the user can adapt the number a cartridge carried to his needs.

## Mass

Water	One cart	Total cartridges
water needed for reaction	2.26638	11.33188 kg
unreacted wat	0.67991	3.399565 kg
cycled water	1.26917	6.345854 kg
non cycl wat (carried)	0.99721	4.986028 kg
Chemical Mass at start	One cart	Total cartridges
LiH at start	1	5 kg
non cycl wat (carried)	0.99721	4.986028 kg
total chemical mass	1.99721	9.986028 kg
Chemical Mass at end		
unreacted LiH	0.3	1.5 kg
unreacted wat	0.67991	3.399565 kg
LiOH prod	2.10895	10.54474 kg
total chemical mass	3.08886	15.4443 kg
System mass		
all included	2	2 kg

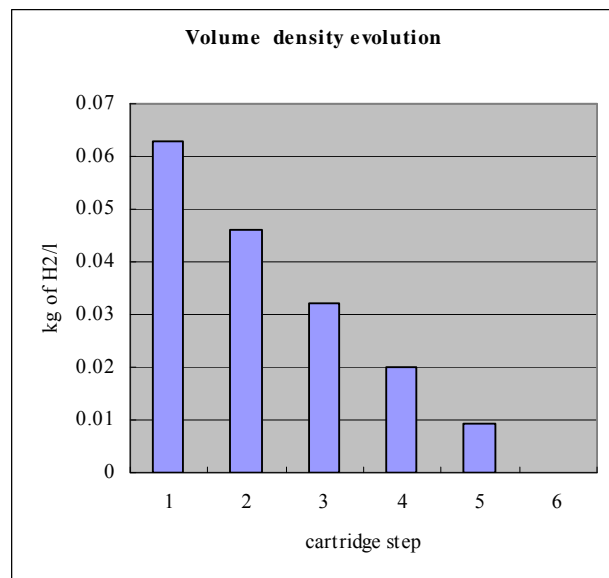
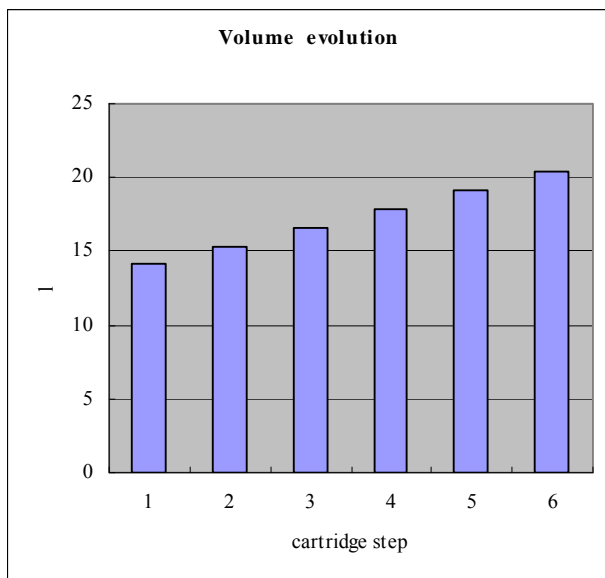


Mass density at start (7%) is about on third lower than pure chemical density (25%). The difference is mostly due to incomplete water (5 kg) recycling and to system mass (2 kg). Those are parameters that can be improved with future developments.

Mass increase with usage is mostly due to hydroxide weight, which is an intrinsic limit to system density in use.

## Volume density

System Volume	One car	Total cartridges
Powder tank volume	2.4075	2.40747 l
Water tank volume	4.986	4.98603 l
Other volumes	1	1 l
<b>Total hydrolyser</b>	<b>8.3935</b>	<b>8.3935 l</b>
<b>volume of a new cartrid</b>	<b>1.1416</b>	<b>5.70776 l</b>
<b>Volume of an old cartri</b>	<b>2.4075</b>	<b>12.0374 l</b>



Volume density at start (0.063 kg of H<sub>2</sub>/l) is a third of that of the pure chemical l (0.2 kg of H<sub>2</sub>/l). Indeed, total volume of 5 fresh cartridges is about 6l, compared a system volume of 6l. In addition, in one cartridge, almost half of the space is void between grains. Those are also parameters that can be improved with future developments.

## 2. Flow control

### Maximal sustainable output

Maximum sustainable output is the maximum output flow that the supply is able to sustain.

It is clear that one advantage of LiH is the powerful output, probably sufficient for a 350 W FC. However, the control of hydrolysis rate is yet to be obtained. This should be one of R&D priorities.

Output-flow depends primary on hydrolysis reaction rate and, on active surface in the cartridge (which includes LiH grain size and cartridge dimensions). To obtain 350 W out of the fuel-cell, it

should be no lower than  $\sim 0.35 \text{ Nm}^3/\text{h}$ , or  $\sim 0.1 \text{ l/s}$  (40% FC efficiency taken into account).

### **Supply dynamics**

Supply dynamic first depends on the delay for hydrolysis reaction to stabilize after opening water input, and after closing water input.

Stop delay should be short enough not let the pressure rise inside tank (to relief valve pressure). Start delay should be compatible with the delay expected on the FC (typically several seconds).

In addition, the system has a buffering capacity which corresponds to the amount of  $\text{H}_2$  gas storable in the hydrolyser. This will enable fast transient over and under demands. Real demand is expected in the range 0 to  $1 \text{ Nm}^3/\text{h}$ .

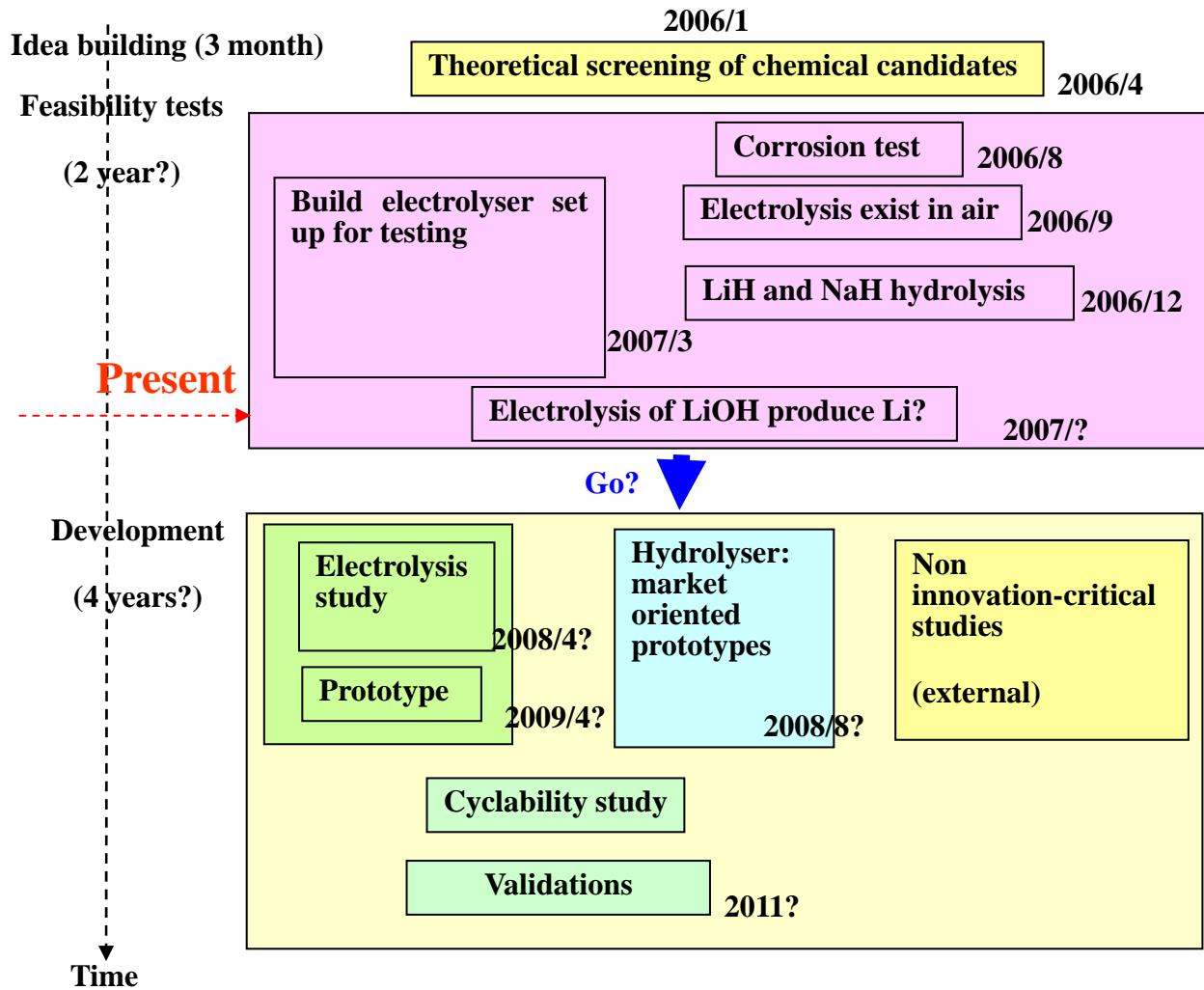
For instance, we may assume that 1 liter of free volume for gas is available in the hydrolyser. If average pressure is set at 4 bar, a  $1 \text{ Nm}^3/\text{h}$  transient can be endured for 14 second by the buffer. Similarly, if system runs at  $0.35 \text{ Nm}^3/\text{h}$  and output is suddenly closed at 4bar, stop delay should be faster than 41s, not to rise over 8 bars.

### **Conclusions of this example**

In this example, the density of the supply system is excellent compared to other  $\text{H}_2$  solutions (see graph on page ). Compared to a standard type I cylinder, this system offers a density improvement of one order both for mass and volume. In addition, the user can adapt the number of cartridge carried to his needs.

Compared to discardable aluminium supply, LiH offers both higher densities, and high flow capacity. On the other hand, lithium waste cannot be discarded, which in terms means more chemical to carry and management difficulties associated with recycling.

### 7. Activity Milestones



## Bibliography

### 1. Data sources

1. Handbook of Chemistry and Physics
2. Merks index
3. webelements.com
4. NIST, webbook.nist.gov
5. www.wikipedia.org

### 2. Identified intellectual property

#### 2.1 Production of Li, Na and their hydrides by electrolysis

1. Method of producing lithium (1967), US3344049 A, (one example of LiCl electrolysis)
2. Electrolytic production of lithium metal, K Sintim-Damoa et al. (1984) US4,455,202 (Electrolysis Li<sub>2</sub>O with LiF)
3. Electrolytic method for the production of lithium using a lithium-amalgam electrode, JF Cooper et al. (1979) US 4,156,635 (aqueous LiOH electrolysis with mercury)
4. Method for electrochemically producing an alkali metal from an aqueous solution (2002) BASF US6770187 B1 (Claims one type of aqueous electrolysis of LiOH)
5. Hydrogen assisted electrolysis processes (2003) Millenium cell & Air products, WO2003078696 A1 (Claims electrolysis of NaOH in presence of hydrogen at the anode)
6. Processes for separating metals from metal salts (2005) Millenium cell (Claims electrolysis of metal borates)

#### 2.2 Production of Li, Na and their hydrides by thermo-reduction

1. Production of lithium hydride (1944) metal hydrides inc US2408748 A (Claims reduction of several lithium compounds to Li with silicon, and then hydrogenation to LiH. There is also a mention to hydrogen feeding during electrolysis.)
2. System for extracting sodium metal from sodium hydroxide with methane as a reductor (1999) Powerball industry inc, US6221310 B1 (Claims system for reduction of NaOH to Na by methane)

#### 2.3 Hydrogen supply by hydrolysis

1. Regeneration of hydrogen storage system materials and methods including hydrides and hydroxides (2004), US20050191235 A1 (Claims hydride + hydroxide => oxide + hydrogen reaction), related patents US20050191234 A1 and US20050191232 A1
2. Production of hydrogen, acetylene and ammonia gases from lithium reaction with hydrocarbon materials (1980) Westinghouse electric corp. US4317659 A (Claims dried biomass + molten Li => LiH, Li<sub>2</sub>C<sub>2</sub>, then hydrolysing. This is an early reference to LiH hydrolysis reaction.)
3. Method for producing gaseous hydrogen by chemical reaction of metals or metal hydrides subjected to intense mechanical deformations (2000) Hydro-Quebec US6572836 B1 (Claims mechanical treatment to form nanocrystal, prior to hydrolysis of hydrides)

#### 2.4 Hydrolyser system

1. A method and apparatus for manufacturing hydrogen generating material, hydrogen generating material, and method and apparatus for generating hydrogen (2004), JP2004107116 A (Claims forming a coil of LiH or NaH for controlled reaction with water)
2. Hydrogen generator (2004) Lynntech inc, WO2005005311 A2 (Claims catalyst control method in hydrolysis reaction of hydrides)
3. Thermally efficient hydrogen storage system (2002) US20030162059 A1 (Claims the combinaison of endothermic and exothermic system to supply hydrogen.)
4. System for generating hydrogen (1997), The Penn state research foundation, US5867978 A (Claims several systems using the hydrolysis of melted lithium and aluminium hydrides)

#### 2.5 Chemical packaging

1. Storage, generation, and use of hydrogen (2002) Safe hydrogen LLC, WO2002066369 A1 (Claims the mix of hydride with carrier liquid and dispersant.)
2. System for hydrogen storage and generation (2005), US20060042162 A1 (claims encapsulation of several hydride to supply hydrogen)

#### 2.6 Other intellectual property

1. Method of hydrogen generation for fuel cell applications and a hydrogen generating system (2001), EP1284922 B1, McGill university (Claims metal hydride + alcohol -> hydrogen reaction)
2. Apparatus and method for refining alkaline solution (2002) Tsurumi soda ltd, US6890417 B2 (Claims electrolytic method to refine NaOH solutions)
3. Electrolytic production of hydrogen (2002) US20030089620 A1 (Claims production of hydrogen by electrolysis of hydrocarbons in presence of NaOH.)

### 3. Scientific literature

#### 3.1 Chemical storage generalities

1. Hydrogen gets onboard, RSC chemistry world march 2006, M. Gutowski, T. Autrey
2. Filling up with hydrogen, C&EN august 22 2005, M. Jacoby
3. An overview of chemical hydrides, B. D. James, Directed technologies inc. ORNL hydrogen storage workshop may 7-8 2003
4. Hydrogen storage and delivery by reversible hydrogenation of liquid-phase hydrogen carriers, A.C. Cooper et al., Corporate Science and



Technology center and advanced materials division Air Products and Chemicals inc

5. Bottling the hydrogen genie, F.E. Pinkerton and B.G. Wicke, the industrial physicist

### 3.2 Lithium production and market

1. Toward new technologies for the production of lithium, G.J. Kipouros and D.R. Sadoway, JOM May 1998 (include one mention to LiOH electrolysis)
2. The lithium industry: its recent evolution and future prospects, A. Ebersperger et al., Resources Policy 30 (2005) 218-231
3. Lithium, J.A. Ober, US geological survey, mineral commodity summaries, January 2006
4. Lithium, J.A. Ober, US geological survey, mineral yearbook, 2004
5. Lithium yearend average lithium price, J.A. Ober, US geological survey, 1999
6. New lithium hydroxide source hits market, Lube report, L. Tocci, Nov. 30 2005 [www.imakenews.com/lng/e\\_article000494041.cfm?x=b11,0,w](http://www.imakenews.com/lng/e_article000494041.cfm?x=b11,0,w)
7. Contribution to the lithium recovery from brine, AH Hamzaoui et al., Desalination 158 (2003) 221-224

### 3.3 Lithium security

1. Fiche toxicologique 183, CDU lithium et composés minéraux, Institut national de recherche et de sécurité

### 3.4 Electrolytic reactions in the Li-O-H system

1. Electrochemical reduction of uranium oxides in Li<sub>2</sub>O-LiCl molten salt, JM Mok et al., p 355, Korea atomic energy research institute
2. LiH to Li (no mistake) by electrolysis [www.chemguide.co.uk/inorganic/group1/compounds.html](http://www.chemguide.co.uk/inorganic/group1/compounds.html), J. Clark 2005
3. Carbon dioxide control: lithium hydroxide, E. Atwater (1996), [oregonstate.edu/~atwaterj/lioh.html](http://oregonstate.edu/~atwaterj/lioh.html)

### 3.5 Other Reactions in the Li-O-H system

1. A literature review of reactions and kinetics of lithium hydride hydrolysis, C. Haertling, R.J. Hanrahan, R. Smith, Journal of nuclear materials 349 (2006) 195-233
2. Structural evolution of LiOH: evidence of a solid-solid transformation toward Li<sub>2</sub>O close to the melting temperature, J. Kiat et al., Sol State comm. 108, 4, 241-245, 1998
3. Kinetic measurement and prediction of the hydrogen outgassing from the polycrystalline LiH/LiOH system, LN Dinh et al., march 24 2005, UCRL-proc-210786
4. Catalytic and inhibiting effects of lithium peroxide and hydroxide on chlorate decomposition, J. Cannon and Y. Zhang, Ind. Eng. Chem. Res. 1995, 34, 3146-3148 (indicates LiOH.H<sub>2</sub>O dehydration at 150C by TGA analysis)

### 3.6 Safe hydrogen LLC publications (LiH-LiOH cycle with organic slurry and carbon reduction regeneration)

1. Could slurry be an answer to hydrogen infrastructure challenge?, Diesel Progress north American edition Nov. 2003, B. Siuru (Safe hydrogen LLC)
2. Hydrogen transmission/storage with a metal hydride-organic slurry and advanced chemical hydride/hydrogen for PEMFC vehicles, proceed. of the 2000 US DOE hydrogen program review, A. McClaine, R.W. Breault, C. Larsen, R. Konduri, J. Rolfe, F. Becker, G. Miskolcsy, Thermo technologies a thermo electron company (ex Thermo Power Corporation?)
3. Technical assessment and analysis of hydrogen R&D projects, Proceedings of the 1999 US DOE hydrogen program review, E.G. Skolnik, J.P. Dipietro, and Z.U. Haq, Energetics incorporated
4. Hydrogen transmission/storage with a metal hydride/organic slurry, proceed. of the 1998 US DOE hydrogen program review, R.W. Breault, J. Rolfe, and A. McClaine, Thermo Power Corporation

### 3.7 Lithium nitride storage

1. Interaction of hydrogen with metal nitrides and imides, P. Chen et al., Nature, vol 420, 21 nov. 2002
2. Mechanism of novel reaction reaction from LiNH<sub>2</sub> and LiH to Li<sub>2</sub>NH and H<sub>2</sub> as a promising hydrogen storage system, T. Ichikawa et al., J. Phys. Chem. B, 108 (23), 7887-7892, 2004
3. Ultrafast reaction between LiH and NH<sub>3</sub> during H<sub>2</sub> storage in Li<sub>3</sub>N, Y.H. Hu and E. Ruckenstein, The journal of phys chem. A, 107, 46, (nov. 20 2003)
4. Lithium nitride based materials for hydrogen storage, L.L. Shaw et al., 2005 DOE hydrogen program review (powerpoint document)

### 3.8 LiBH<sub>4</sub> storage

1. Hydrogen generation by hydrolysis reaction of lithium borohydride, Y. Kojima, et al., International journal of hydrogen energy 29 1213-1217 (2004)
2. Hydrogen purification and storage using lithium borohydride, Nasa project statement of work 2003-2004, C.A. Linkous, florida energy center

### 3.9 Sodium

1. Low-cost off board regeneration of sodium borohydride, DOE hydrogen program, FY 2004 progress report III.B.1, Y. Wu, M. T. Kelly, J. V. Ortega, Millenium cell inc.
2. Process for the regeneration of sodium borate to sodium borohydride for use as a hydrogen storage source, Y. Wu, Millenium cell inc., May 24 2005
3. Sodium its manufacture properties and uses, Marshall Sittig 1956, Reinhold

## 4. Related AL internal reports

### 4.1 Chemical storage

1. Hydrogen supply and energy storage through the reaction of light hydrides: Technical assessment, T. Laude, May 25, 2006, ref R1106

2. Technical and economical evaluation of the various chemical hydrides available for hydrogen storage, Nesshy project deliverable, Avril 2006, A. Cuni Air Liquide RR 2006-48
3. Horizon hydrogene energie, projet mobilisateur pour l'innovation industrielle, dossier de presentation du PMII 2006
4. What market for chemical storage? Collaborative document (coordination T. Laude), in progress

#### **4.2 LiH**

1. LiOH electrolysis, T.Laude, in progress

#### **4.3 NaBH<sub>4</sub>**

1. Generation of hydrogen through the hydrolysis of NaBH<sub>4</sub> : Technical state of the art, A. Cuni, 06/04/2006 RR 2006-47
2. Rapport de stage B. Orsal NT 233-2004 (price of NaBH<sub>4</sub>)
3. NaBH<sub>4</sub> technico-economical assessment (logistic & system), K. Barral 2004/10/19 ref 238-2004
4. NaBH<sub>4</sub> stability assesments-intermediate report, K Barral, S. Moreau, P. Renault, 2004/04/11 085/2004

#### **4.4 Aluminium**

1. Hydrogen supply by aluminium hydrolysis, T. Laude R2007 (September 2007)