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hydrogen su ige, a es, ıy



## Summary

Hydrogen can be supplied by an activated aluminium hydrolysis reaction:  $2 \text{ Al} + 6\text{H}_2\text{O} => 2\text{Al}(\text{OH})_3 + 3\text{H}_2$ . This is a potential supply solution for fuel-cell customers, or for Industrial Merchant hydrogen customers. Aluminium can also be used as a commodity for storage and distribution, especially where water is available at supply point.

Aluminium offers a relatively high density solution, especially for volume. Aluminium is readily available from the aluminium industry. The chemical cost of aluminium is around 17\$ per kg of hydrogen supplied (1.2\$/Nm<sup>3</sup>), which is reasonable in a hydrogen distribution framework comparable to that of present Industrial Merchant market. There is however a CO<sub>2</sub> emission drawback from aluminium production. Also, hydrolysis needs activation to remove the passivating hydroxide layer that naturally occurs on Al metal. Several activation solutions exist, in particular mixing aluminium with soda (NaOH).

Strategically, several actors have recently taken positions in the field, in particular Hitachi and Air Products. However their intellectual property position is not yet confirmed, and may not be.

All in all, aluminium offers a solution that is not the highest among chemicals, either for cost or density, but that has reasonable technical barrier (mostly hydrolysis activation) and relatively low business barrier. An essential advantage of aluminium compared to other chemicals is that the supply chain can be built upon existing aluminium industry where recycling and reprocessing of Al is widely practiced. Hence, it is a solution that may be available on short to mid terms.

Although the business model for AL is closer to aluminium cartridge reselling than to direct gas supply, it should be understood that in the mid term, aluminium should be replaced by hydrogen consuming chemicals, such as LiH. We believe that hydrogen consuming chemicals require longer development, but will eventually be more performing than aluminium.

We therefore believe that the early development of an aluminium solution is of strategic importance.



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Reminder:

Stable Compounds of Al-O-H system: Al, AlH<sub>3</sub> (tends to be instable), Al(OH)<sub>3</sub>, AlOOH, Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O, H<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>

## 1. The concept

H2 can be supplied by reacting water with aluminium, with the reaction:

$$2AI + 6H_2O = activation => 2AI(OH)_3 + 3H_2$$
 (1)

In a few words:

- Cheap compounds (recycling is optional)
- ➢ Good storage density, especially in volume (although average as a chemical solution)
- > Need to activate the hydrolysis (to remove passivating hydroxide layer).
- Low technical risk solution

Aluminium hydrolysis can be used either as a supply solution for a fuel-cell customer, or for an Industrial Merchant H2 customer.

Aluminium can also be used as a commodity for storage and distribution. In many case, water storage and distribution does not need to be considered as it is readily available at supply point.

In addition, in mobile fuel-cell systems, water output from the fuel cell can partially be recycled to the hydrolyser, for storage density improvement.

Potential business model for Air Liquide:

- Aluminium cartridges distribution and sales as a H2 supply
- > Equipment and service sales (e.g. hydrolyser and activator)

Potential profits for Air Liquide:

- Increased sales by competitive advantage
- Reduced distribution costs
- New equipment and service sales

We do not consider hydrolysing using AlH<sub>3</sub> instead of Al, because AlH<sub>3</sub> would deprive from the main interest of the aluminium solution: cheapness (thanks cheap production and well established supply



infrastructure). AlH<sub>3</sub> can be hydrolysed (AlH<sub>3</sub> + 3  $H_2O$  -> Al(OH)<sub>3</sub> + 3  $H_2$ ) and offers a better energy density than aluminium. However, AlH<sub>3</sub> cannot be synthesized by the direct reaction of aluminium with  $H_2$ . Instead, aluminum hydride is usually prepared as a solution by the reaction of lithium aluminum hydride with aluminum trichloride. A. E. Finholt et al. (1947) J. Chem. Soc. 69:1199, which is not as cost efficient.

## 2. Storage density

## 2.1 Pure chemical density

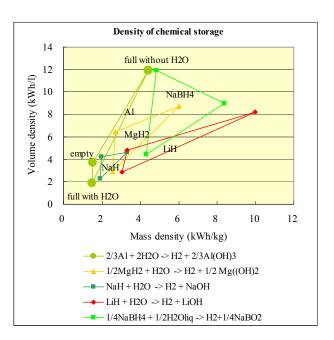
|            |                     | 2/3Al + 2H2O -> H2 + 2/3Al(OH)3 |                 |                 |  |
|------------|---------------------|---------------------------------|-----------------|-----------------|--|
|            |                     | F                               | Full            |                 |  |
|            |                     | No water                        | With water      |                 |  |
|            | Compared            | H2/(2/3Al)                      | H2/(2/3Al+2H2O) | H2/[2/3Al(OH)3] |  |
| Mass       | kg of H2/kg         | 11.21%                          | 3.73%           | 3.88%           |  |
| density    | kWh/kg              | 4.414                           | 1.470           | 1.527           |  |
|            | MJ/kg               | 15.890                          | 5.291           | 5.496           |  |
| Volume     | kg of H2/l          | 0.302801004                     | 0.047222169     | 0.093808094     |  |
| density    | kWh/l               | 11.927                          | 1.860           | 3.695           |  |
|            | MJ/l                | 42.936                          | 6.696           | 13.302          |  |
| Dimensions | mass (kg/kg of H2)  | 8.923                           | 26.797          | 25.797          |  |
|            | volume (l/kg of H2) | 3.302                           | 21.176          | 10.660          |  |
|            | (no void)           |                                 |                 |                 |  |

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

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).

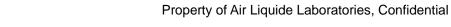
Hence, pure chemical density can be described as 3 points:





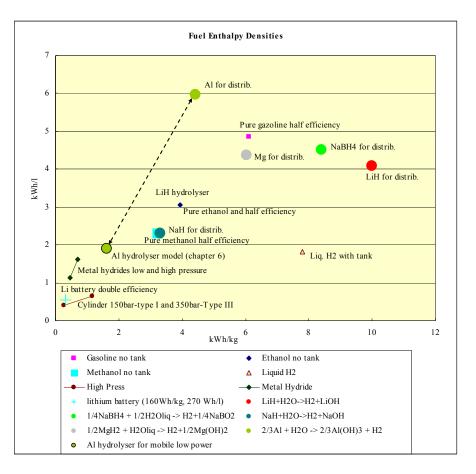
If comparing pure chemical density, aluminium is rather average among other chemical solutions for mass density, but is excellent for volume density if water is not carried.

However this simple comparison is not conclusive as each chemical is affected differently by other factors in the practical application as a  $H_2$  storage media.





## 2.2 Real densities



Hypothesises:

- 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 (last chapter)
- For liquid hydrocarbon, density does not include tank and liquid densities (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 <u>http://en.wikipedia.org/wiki/Lithium\_ion\_battery</u>) density are doubled to account for the fact that electricity can be converted efficiently to useful energy.
- Cylinder type I is 15kg, 10 liter (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 pressure MH (7.3kg H<sub>2</sub>, 420kg, 180l, 350bar)
- Liquid  $H_2$  is assumed 20% $H_2$ mass, and +30%non $H_2$  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. It is clear that chemical density is remarkable for any chemical, but aluminium performs better for volume than for mass.



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 modelization 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. Although not important for aluminium, 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], but also of LiH [LiOH.H<sub>2</sub>O hydrate].

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.

Considering a mobile low-power application (last chapter), density performance of the aluminium hydrolyser is of course far lower than its density for distribution, however it still compares favorably to other supplies.

## 3. Business validity: Aluminium cost

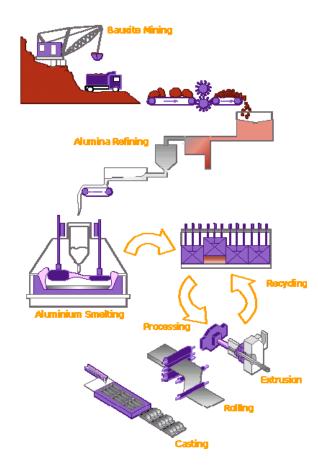
The industry of aluminium is long known and highly optimized. It is based on the electrolysis of alumina (Hall-Héroult process 1886):

$$2 \operatorname{Al}_2 \operatorname{O}_3 + 3 \operatorname{C} \to 4 \operatorname{Al} + 3 \operatorname{CO}_2 \qquad (2)$$

Process (Quote from <u>http://world-aluminium.org</u>): Bauxite is first refined into aluminium oxide trihydrate (alumina). Then alumina is dissolved in an electrolytic bath of molten cryolite (sodium aluminium fluoride) within a large carbon or graphite lined steel container. An electric current is passed through the electrolyte at low voltage (3-5V), but very high current, typically 150,000



amperes. The electric current flows between a carbon anode (positive), made of petroleum coke and pitch, and a cathode (negative), formed by the thick carbon or graphite lining of the pot. Molten aluminium is deposited at the bottom of the pot and is siphoned off periodically. A typical aluminium smelter consists of around 300 pots. These will produce some 125,000 tonnes of aluminium annually.



The market price of aluminium metal was 1.94 \$/kg in 2005 US, but it is rather fluctuant. Production cost is around 1.22 \$/kg, and declining thanks to technological progresses. This cost includes alumina 38% (0.46\$/kg), electrical power 29%, and carbon 10%. (CRU strategies)

Considering that we need 8.92 kg of aluminium for 1 kg of H<sub>2</sub>, the metal cost to store hydrogen is straightforward:

| \$/kg of H2 | \$/Nm3 of H2 | \$/kWh of H2 |
|-------------|--------------|--------------|
| 17.31       | 1.20         | 0.439        |

Note: It is possible to consider Al(OH)<sub>3</sub> recycling if selling back to the aluminium industry. Al(OH)<sub>3</sub> is a close compound of alumina, which is worth 0.46\$ per kg of Al element, hence 0.46x8.92 = 4.1\$ per kg of H<sub>2</sub> supplied. However the cost of collecting the waste product (rather than discarding



it) should be estimated. Today, a large infrastructure is already in place to recycle waste aluminium metal, that accounts for about one third of aluminium production.

Aluminium cost of the solution should be compared to:

1. The cost of hydrogen.

We may assume the following prices: (from AL 2006 AII report p.31, and A. Leon, conversion 1 eur = 1.2 \$)

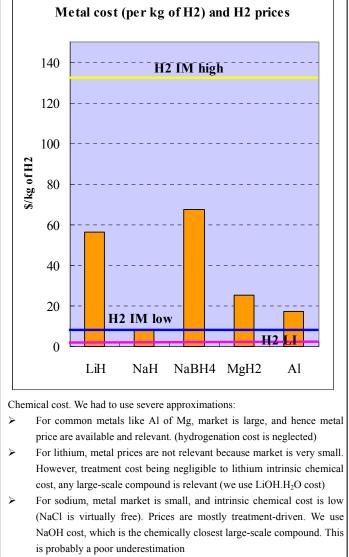
- > Large Industry ~ 2.7 kg, (0.24  $\text{Mm}^3$ )
- ▶ Industrial Merchant: 8.7 to 133 \$/kg (0.78 to 12 \$/Nm<sup>3</sup>)

It is clear that aluminium cost is large compared to hydrogen production cost. However, metal cost is not large compared to distribution and processing costs of some existing IM hydrogen customers today. In addition, it should be considered the eventual saving on the distribution costs thanks to density and usability of the chemical solution.

For future hydrogen energy market, 17.3\$ per kg (1.2 \$/Nm<sup>3</sup>) of hydrogen supplied can be seen as an incompressible cost for this solution. This would probably limit its application to markets where price constraint is not critical (small volume consumers).



## 2. The cost of other chemical solutions



| $\triangleright$ | For NaBH <sub>4</sub> , minimal future cost has been estimated in a different AL |   |
|------------------|--|---|
|                  | study (conversion, $1 \text{ eur} = 1.2 $ ).                                     | l |

| Element              | \$/kg       |
|----------------------|-------------|
| Li as LiOH.H2O       | 14.3        |
| Li as LiCO3          | 14.0        |
| Na as NaCO3          | 0.397       |
| Na as NaOH           | 0.696       |
| Na as Na2SO4         | 0.456       |
| Na as NaCl           | 0.0178      |
| Mg as MgO            | 0.663       |
| Mg as Mg(OH)3        | 2.115965903 |
| Mg as MgCl2          | 1.101123209 |
| Mg as Mg             | 3.858E+00   |
| Be as Be(OH)2        | 54.04405306 |
| Be as Be             | 1.400E+02   |
| Al as Al2O3          | 0.700982777 |
| Al as Al             | 1.940E+00   |
| B as Na2B4O7.5H2O    | 2.695E+00   |
| NaBH4 present        | 40 eur/kg   |
| NaBH4 minimal future | 12 eur/kg   |

Source: US geological survey, except NaBH4 (AL internal study of B. Orsal)

Compared to other chemical solutions, there are two other similar solutions that have comparable cost-efficiency: NaH and MgH<sub>2</sub> (or their mix). NaH is not competitive for density, and raises security issues due to very active hydrolysis.  $MgH_2$  is a viable alternative, although more expensive raw material.

## CO<sub>2</sub> environmental cost

 $CO_2$  is released during the production of aluminium. For hydrogen produced from aluminium, the theoretical  $CO_2/H_2$  mass-ratio of 10.9 (this is deduced only from reaction (1) and (2)).



A more complete production-based evaluation gives a  $CO_2/H_2$  mass-ratio as high as 17.8. This is based on  $CO_2/Al$ mass-ratio of 1.6 for the smelting process а (http://world-aluminium.org/Sustainability/Environmental+Issues/Greenhouse+gases, not including indirect CO<sub>2</sub> emissions such as from electricity production), and the assumption of 80% chemical efficiency for aluminium hydrolysis.

For comparison, this is notably higher than SMR hydrogen production ( $CH_4 + H_2O \rightarrow CO + 3 H_2$ , then  $CO + H_2O \rightarrow CO_2 + H2$ ), where theoretical  $CO_2/H_2$  mass-ratio is 5.46, and where a more complete production-based evaluation gives a  $CO_2/H_2$  mass-ratio of 9.34 (data come from an existing plant and include indirect  $CO_2$  such as produced from heating).

Obviously,  $CO_2$  emission is an issue in the mid term for  $H_2$  production by aluminium hydrolysis. However, this may not be a fatal issue for small volume production, such as for Industrial Merchant markets.

Note: There is also an issue of  $CF_4$  emission from aluminium industry. However, this issue is progressively being tackled, and may not be critical in the future.

## 4. Technical validity: Activation of the hydrolysis of aluminium

Aluminium can reduce hydrogen from water (2 Al +  $6H_2O \Rightarrow 2Al(OH)_3 + 3H_2$ ) because of its positive oxidation potential, but does not normally do so because of the protection by a surface layer of hydroxide and/or oxide. This layer does not crack when it is formed. In addition Al(OH)\_3 is insoluble in water.

However, there are several ways to activate the hydrolysis reaction:

Mixing with a cheap base, typically NaOH to remove the passivating layers of Al(OH)<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub>:

 $Al(OH)_3 + NaOH \Longrightarrow Na^+ + [Al(OH)_4]^-$ 

and  $Al_2O_3 + 2NaOH + 3H_2O => 2Na^+ + 2[Al(OH)_4]^-$ 

According to literature, NaOH is not consumed by this reaction. The reason is that  $Al(OH)_3$  partly precipitates from  $[Al(OH)_4]^-$ . Hence the effect of NaOH on Al hydrolysis is catalytic in nature.

For this reason only a small amount of NaOH may be needed in the storage.

Here follows a visual demonstration.



(from http://www2.uni-siegen.de/~pci/versuche/english/v44-10.html)



Materials used



40 percent sodium hydroxide solution



After approx. 2 minutes





End of the reaction

One alternative to direct mixing with NaOH, is to mix aluminium with Na or NaH powder. During hydrolysis, NaH or Na are converted to NaOH (also releasing hydrogen and heat).

Mixing with calcium oxide (Hitachi-Masao Watanabe technique)

Calcium oxide is reported by Hitachi to act as a heat provider when reacting with water: CaO +  $H_2O \leftrightarrow Ca(OH)_2$ . However, it is likely that the basic calcium hydroxide acts in the same way as NaOH. In Hitachi's patent, powder is grinded to a powder below 60 microns.

> Mixing with a cheap acid typically HCl is also possible

 $Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$ 

As opposed to NaOH, this reaction probably consumes HCl.

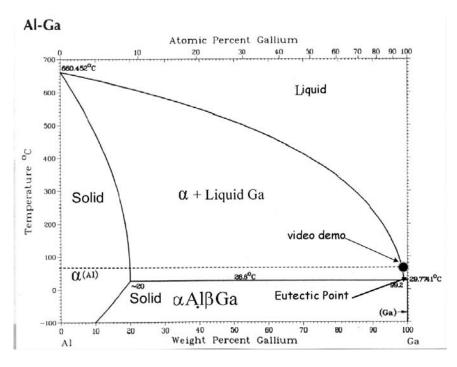
Mixing with usual salts: NaCl, KCl

This is reported to activate de reaction by a pitting mechanism of the  $Al(OH)_3$  layer. Although the mechanism is not fully understood, it possibly involves the partial solubilization of the  $Al(OH)_3$  layer.

Mixing with gallium (or mercury) (Purdue university work [3.2.2.3])

Gallium and aluminium form an eutectic (see figure). Over 26C, a few percent of aluminium can be dissolved in gallium. Dissolved aluminium in liquid gallium is then reactive with water. This is sought to be used as a hydrogen supply technique. However the process of efficiently dissolving large quantities of aluminium is to be clarified. Also, gallium should be recycled rather than discarded, which imposes an additional process.





From [3.2.2.3]

## 5. IP validity and known actors

### **5.1 IP Situation**

Although the hydrolysis of aluminium is well known chemistry, there has recently been a trend to take IP positions by several actors, submitting various patent applications. All applications are at first stage (A1). Considering the simplicity of the processes involved, it is not clear if such patenting will be successful.

- Hydrolysis with NaOH (including the description of an hydrolyser): Method for producing hydrogen (filed Dec 16 2002) Mario Theriault US2003/0143155 A1
- Hydrolysis with salts (NaCl, KCl,...): Compositions and methods for generating hydrogen from water (filed April 9 2004) McDermott Will & Emery LLP, US2005/0232837 A1
- Hydrolysis metal + base + borohydride: Combination metal-based and hydride-based hydrogen sources and processes for producing hydrogen, (filed June 17<sup>th</sup> 2005) H<sub>2</sub> Volt Inc., WO2006/009927 A1
- Hydrolysis with fine aluminium grains and calcium oxide (and related) Hydrogen generating material, hydrogen generator and fuel cell, (filed dec 28<sup>th</sup> 2005) Hitachi Maxell EP1757557A1
- Hydrolysis with NaOH (claimed only based on PH>12...): Method for generating hydrogen gas (filed July 19<sup>th</sup> 2006) Air Products and chemicals, EP1749796A1

As today, AL has not developed a hydrogen storage or activation method. We need further



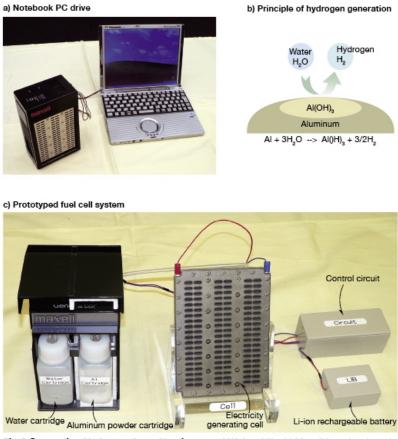
development before determining an IP strategy.

We believe that the first priority is to master the hydrolysis technology, and then to secure intellectual property where possible. It may be tentatively assumed that this solution will stay mostly IP opened in the future.

## 5.2. Reported prototype hydrolysers

Today, only Hitachi and its collaborator, Prof. Masao Watanabe of Muroran Institute of technology, have publicly reported aluminium-based hydrolysers. Prof. Watanabe is running his own venture company (Hydro-device co), hence Hitachi models and Hydro-device co models are different.

According to Hitachi patent report, the chemical is probably finely ground aluminium powders, mixed with calcium oxide.



**Fig 2 Generating Hydrogen from Aluminum and Water** Hitachi Maxell has developed a fuel cell system that reacts aluminum powder with water to generate hydrogen fuel, which is then used to generate electricity (a). Specially-processed aluminum is reacted with water to generate 1.3L of hydrogen from 1g of aluminum and 2g of water at room temperature (b). The prototype system (160 x 100 x 60mm, 920g) attains 10W average output, with peak 20W. Voltage is 7.4V. The electricity generating cell uses a fluorine-based solid polymer electrolytic membrane (c).

First 10W Module (Hitachi)

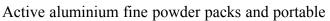




2006, 10W Module (Hitachi)



hydrolyser (Hydro-device co)





Mobile hydrolyser (Hydro-device co.)

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

The following example is given for better conceptualisation, but should not be understood as a mature development.

## Need

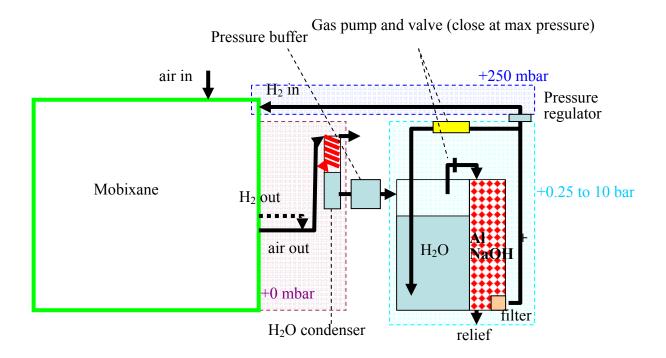
We need a storage/supply system to be coupled with a low-power/mobile generation system. Today,



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:

- ▶ H2 purity compatible with a fuel cell
- ➢ Constant pressure +250mbar on FC input
- Stable flow between 0 and 0.35  $\text{Nm}^3/\text{h}$  (about 0 to 0.35 kW considering 40% FC efficiency)
- > Transient flows on FC input up to  $1 \text{ Nm}^3/\text{h}$
- Stabilisation time compatible with the FC (3.5s for start up)
- Massic and volumic density superior to cylinder type I solutions
- ➢ Volume around 101
- Ease of use and security



## **Technical Solution**

- > Powder is dry aluminium mixed with a limited amount of NaOH.
- Powder is packaged as discardable cartridges ("tea-bag" type) under a sealed packaging (to protect from moisture). They can be discarded to municipal waste after use.
- > 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  $H_2$  recirculation



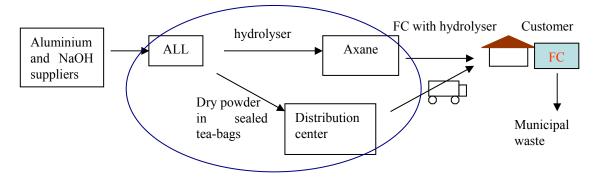
system that closes over a given pressure.

- Water input is from tank top to maximize reacted powder. Cross section of the cartridge is adapted to output flow.
- $\succ$  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

Modelisation is based on the followings hypothesizes:

| FC water recycling rate     | 0.8  |            |                 |           |        |
|-----------------------------|------|------------|-----------------|-----------|--------|
| NaOH/Almass rate            | 0.05 |            |                 |           |        |
| reaction complet rate       | 0.8  | Stoichiome |                 |           |        |
| number of cartridge         | 5    |            |                 |           |        |
| Al mass 1 one cartridge     | 1    | kg         |                 |           |        |
| System mass                 | 2    | kg         |                 |           |        |
| Min available H2 volume     | 1    | 1          | Cylinder type I | for compa | arison |
| Set pressure for water stop | 4    | bar        | mass            | 15        | kg     |
| Non-tank volumes            | 1    | 1          | pressure        | 150       | bar    |
| Powder volume ratio         | 0.6  |            | volume          | 10        | 1      |
| FC efficiency               | 0.4  |            | H2 density      | 9.1612    | kg/m3  |

### Autonomy

| Autonomy         | kg H2   | Nm3      | kWh FC out  |
|------------------|---------|----------|-------------|
| 1 cartridge      | 0.08965 | 1.362499 | 1.412472124 |
| Total cartridges | 0.44826 | 6.812493 | 7.062360618 |

| Cylinder type I (for comparison) |         |         |             |  |  |
|----------------------------------|---------|---------|-------------|--|--|
| Autonomy kg H2 Nm3 kWh FC out    |         |         |             |  |  |
|                                  | 0.09161 | 1.39228 | 1.443345481 |  |  |

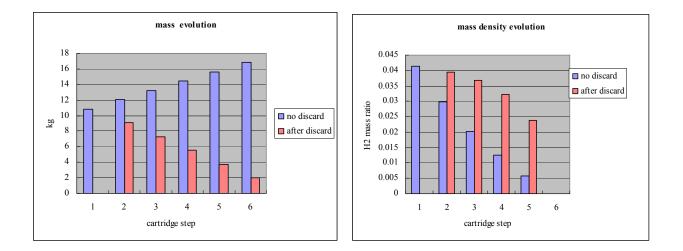
The H2 content of the storage (with 5 cartridges) is about 5 times that of a 10-liter type-I cylinder (which has comparable mass and volume. See below.).

At full power (350W), the autonomy (with 5 cartridges) is 20 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 cart | ridges |
|---------------------------|----------|------------|--------|
| water needed for reaction | 2.00306  | 10.01529   | kg     |
| unreacted wat             | 0.40061  | 2.003058   | kg     |
| cycled water              | 1.28196  | 6.409787   | kg     |
| non cycl wat (carried)    | 0.7211   | 3.605505   | kg     |
| Chemical Mass at start    | One cart | Total cart | ridges |
| Al at start               | 1        | 5          | kg     |
| NaOH                      | 0.05     | 0.25       | kg     |
| non cycl wat (carried)    | 0.7211   | 3.605505   | kg     |
| total chemical mass       | 1.7711   | 8.855505   | kg     |
| Chemical Mass at end      |          |            |        |
| unreacted Al              | 0.2      | 1          | kg     |
| NaOH                      | 0.05     | 0.25       | kg     |
| unreacted wat             | 0.40061  | 2.003058   | kg     |
| Al(OH)3 prod              | 2.31279  | 11.56397   | kg     |
| total chemical mass       | 2.96341  | 14.81703   | kg     |
| System mass               |          |            |        |
| all included              | 2        | 2          | kg     |



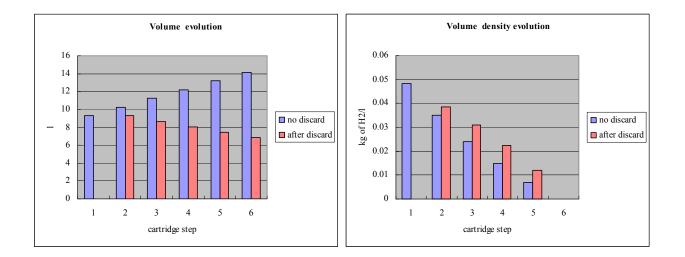
Mass density at start (4%) is about on third lower than pure chemical density (11%). The difference is mostly due to incomplete water (3.6 kg) recycling and to system mass (2 kg). Those are parameters that can be improved with future developments.

Mass increase with usage is mostly due to hydroxide weight, which is an intrinsic limit to system density in use. However, regular cartridge discarding by the user greatly ease this problem.



## **Volume density**

| System Volume            | One car | Total car | tridges |
|--------------------------|---------|-----------|---------|
| Powder tank volume       | 1.5928  | 1.59283   | 1       |
| Water tank volume        | 3.6055  | 3.60551   | 1       |
| Other volumes            | 1       | 1         | 1       |
| Total hydrolyser         | 6.1983  | 6.19834   | 1       |
| volume of a new cartrid  | 0.6168  | 3.08414   | 1       |
| Volume of an old cartrie | 1.5928  | 7.96417   | 1       |



Volume density at start (0.05 kg of  $H_2/l$ ) is a sixth of that of the pure chemical 1 (0.3 kg of  $H_2/l$ ). Indeed, total volume of 5 fresh cartridges is about 31, compared a system volume of 61. 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 not clear if an output sufficient for a 350 W FC can be sustained with aluminium. For comparison, today Hitachi's pocket size prototype hydrolyser (calcium oxide catalyst) is designed for 10W FC. We suggest the hydrolysis rate information to be set as priority of a R&D campaign.

Output-flow depends primary on hydrolysis reaction rate (which includes NaOH activity) and, on active surface in the cartridge (which includes aluminium grain size and cartridge dimensions). To obtain 350 W out of the fuel-cell, it should be no lower than ~ 0.35  $\text{Nm}^3/\text{h}$ , or ~ 0.1 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  $H_2$  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 Nm<sup>3</sup>/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 competitive to other  $H_2$  solutions (see graph on page 6). Compared to a standard type I cylinder, this system offers a density improvement of a factor 5 both for mass and volume.

In addition, the user can adapt the number of cartridge carried to his needs.

However, there is still an important technical unknown before development: Can the hydrolysis rate of aluminium accommodate the consumption need of a 350 W FC? We believe that is question should be answered by a R&D campaign.



## Bibliography

#### 1. Data sources

- Handbook of Chemistry and Physics
- Merks index
- ➢ webelements.com
- NIST, webbook.nist.gov
- www.wikipedia.org
- 2. Identified intellectual property

#### 2.1 Hydrogen generation by aluminium hydrolysis

- Method for producing hydrogen (filed Dec 16 2002) Mario Theriault US2003/0143155 A1 [Hydrolysis with NaOH including the description of an hydrolyser]
- Compositions and methods for generating hydrogen from water (filed April 9 2004) McDermott Will & Emery LLP, US2005/0232837 A1 [Hydrolysis with salts (NaCl, KCl,...)]
- Combination metal-based and hydride-based hydrogen sources and processes for producing hydrogen, (filed June 17th 2005) H2 Volt Inc., WO2006/009927 A1 [Hydrolysis metal + base + borohydride]
- Hydrogen generating material, hydrogen generator and fuel cell, (filed dec 28th 2005) Hitachi Maxell EP1757557A1 [Hydrolysis with fine aluminium grains and calcium oxide (and related)]
- Method for generating hydrogen gas (filed July 19th 2006) Air Products and chemicals, EP1749796A1 [Hydrolysis with NaOH (claimed only based on PH>12...)]

### 2.2 Other IP

- System for generating hydrogen (1997), The Penn state research foundation, US5867978 A [Claims several systems using the hydrolysis of lithium and aluminium hydrides]
- Thermally efficient hydrogen storage system (2002) US20030162059 A1 [Claims the combinaison of endothermic and exothermic system to supply hydrogen.]

### 3. Scientific literature

### 3.1 Chemical storage generalities

- > Hydrogen gets onboard, RSC chemistry world march 2006, M. Gutowski, T. Autrey
- Filling up with hydrogen, C&EN august 22 2005, M. Jacoby
- An overview of chemical hydrides, B. D. James, Directed technologies inc. ORNL hydrogen storage workshop may 7-8 2003
- 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
- > Bottling the hydrogen genie, F.E. Pinkerton and B.G. Wicke, the industrial physicist

### 3.2 Aluminium

### 3.2.1 Aluminium General

- Aluminum, P.A. Plunkert, US geological survey, mineral commodity summaries, 2006
- Aluminum, P.A. Plunkert, US geological survey, mineral yearbook, 2004
- Abrasive manufactured (Al2O3), D.W. Olson, US geological survey, mineral commodity summaries, 2006
- Abrasive manufactured (Al2O3), D.W. Olson, US geological survey, mineral yearbook, 2004
- Aluminium prices: What should we expect?, CRU Strategies, 72<sup>nd</sup> annual meeting of the aluminium association (2005)
- http://www.world-aluminium.org/
- http://www.du.edu/~jcalvert/phys/alumin.htm

### 3.2.2 Aluminium hydrolysis

- > Maxell develops fuel cells utilizing reaction of aluminium and water for hydrogen generation, report
- Venture of prof Masao Watanabe: <u>http://www.hydro-device.com/en/index.html</u>
- The science and technology of aluminium-gallium alloys as a material for energy storage, transport and splitting water, J M Woodal, Purdue university, ECHI-2 April 12 2007

### 3.2.3 Decomposition 2/3AlH3 => H2 + 2/3Al

- Synthesis and characterization of alanes for automotive applications, Jason Graetz et al. (Brookhaven national laboratory) DOE presentation 05/17/2006 Project #ST 15
- Aluminum hydride, AlH3, as a hydrogen storage compound, Jason Graetz et al. (Brookhaven national laboratory), BNL-77336-2006 formal report
- The potential of alunimum hydride for vehicular hydrogen storage, J. Reilly, et al., (Brookhaven national laboratory) IPHE international hydrogen storage technology conference (2005)

#### 4. Related AL internal reports

#### 4.1 Chemical storage



- > Hydrogen supply and energy storage through the reaction of light hydrides: Technical assessment, T. Laude, May 25, 2006, ref R1106
- 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
- > Horizon hydrogene energie, projet mobilisateur pour l'innovation industrielle, dossier de presentation du PMII 2006
- > What market for chemical storage? Collaborative document (coordination T. Laude), in progress
- 4.2 LiH
- > Hydrogen supply by LiH, T. Laude, in progress
- LiOH electrolysis, T.Laude, in progress
- 4.3 NaBH4
- Seneration of hydrogen through the hydrolysis of NaBH4 : Technical state of the art, A. Cuni, 06/04/2006 RR 2006-47
- Rapport de stage B. Orsal NT 233-2004 (price of NaBH4)
- > NaBH4 technico-economical assessment (logistic & system), K. Barral 2004/10/19 ref 238-2004
- > NaBH4 stability assessments-intermediate report, K Barral, S. Moreau, P. Renault, 2004/04/11 085/2004