# Materials for hydrogen storage

*… a step towards the hydrogen economy ?*

**Members Foresighting Report**
**29th March 2006**

Confidential © iti Scotland Ltd

# Materials for hydrogen storage

**Safe and inexpensive hydrogen (H2) storage is essential for the development of H2 as a commercially viable energy vector. A new class of storage materials can play a key role in helping to achieve this.**

**To be successful, storage materials will require to develop from where they are today by focusing on improving safety, achieving higher specific density and lowering the cost of production.**

**The development of a new class of storage materials, specifically for niche applications, is a possible route forward to increasing the use of hydrogen in commercial applications.**

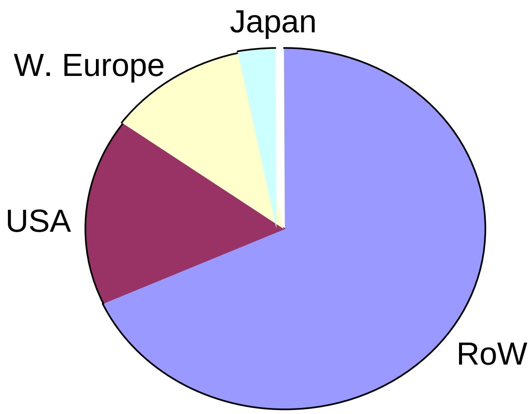
**This short review attempts to explore such paths.**

***Acknowledgements***

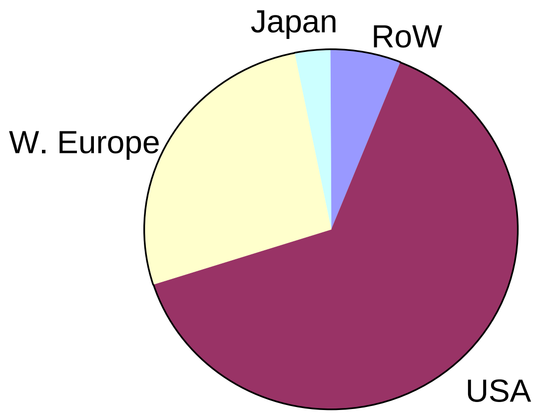
***ITI Energy wishes to thank our members, especially Alterg and Scientific Generics, who have provided input into this short focused review. We look forward to additional comments and views from all interested members. These can be addressed to Michael Weston, michael.weston@itienergy.com***

# Current hydrogen use – overview

## 2003 Captive Hydrogen Market - 43 Mt




## 2003 Merchant Hydrogen Market - 2 Mt




The hydrogen market is split into two distinct sectors, captive and merchant. By volume the captive market accounts for 96% of the market and merchant the remainder.

The captive market relates to installations which have one large scale dedicated consumer, such as a refinery or petro-chemicals plant. In oil refining hydrogen use has increased rapidly over the last 10 years to remove sulphur from diesel, and with increasing requirements for cleaner fuels, this demand is likely to rise. Major applications currently include the manufacturing of ammonia and petro-chemicals (including methanol).

The merchant market relates to smaller scale applications where the hydrogen is delivered via cylinders, multi-cylinder pallets, truck and third party pipeline. Major applications are: Electronics for carrier gas in semiconductor production processes, Glass for heat treatment of hollow glass and optic fibres, Metallurgy for recycling of catalysts and Research laboratories for flame ionisation.

# Why develop H2 storage materials?

**There is increasing evidence that the world energy system will rapidly need to move towards lower net generation of CO2 and, over the very long term, become CO2 neutral. Transport represents about one third of energy related green-house gas (GHG) emissions. Currently, liquid bio-fuels, electricity and hydrogen are seen as potential low or GHG free energy vectors for that sector.**

**The issues surrounding H2 storage are seen by many as critical to the future success of hydrogen based technologies, which would lead to the emergence of "the hydrogen economy". Focus is currently on potential breakthroughs in hydrides and other materials.**

**In the hydrogen economy, H2 storage materials can aim at two distinct, but interlinked targets characteristics:**

- **low cost and relatively low H2 capacity for filling stations**
- **higher cost and high H2 capacity material for on-board storage**

**Both materials must be able to interact via the loading system interface, eg display characteristics making pressure and loading rate compatible.**

# Towards light reversible hydrides

**All the reversible hydrides working around ambient temperature and atmospheric pressure consist of transition metals (eg iron, nickel and cobalt). H2 storage capacity in such materials is lower than 3% wt.**

**Light hydrides, based on much lighter metals such as magnesium, can store up to 8% wt. of hydrogen. However their operating temperature, in the 300°C range, is too high for efficient operation.**

**Complex metal hydrides, such as Alanates, can be made from low cost elements such as sodium, magnesium and aluminium. Their theoretical reversible capacities ranges from 5.6% to 8% wt.**

**However, practical applications are hampered by poor uptake / release kinetics. Catalysts like titanium and zirconium are known to enhance these properties, but better catalysts are needed, to meet acceptable kinetics and while retaining high storage capacity.**

# Challenges facing hydrides

**In order to meet the performance and costs required for a number or early niche applications, hydrides need to:**

- **be able to operate at a lower working temperature**
- **improve capacity, while retaining acceptable kinetics**
- **be produced more cost effectively, by enabling the use of lower grade / purity metal alloys**

**Resolving these challenges requires a better understanding of the reaction mechanisms through which hydrogen is released or taken up. Modelling atomic interactions will contribute to that goal.**

**Finally, finding alternatives to hydrides (Zeolites, Metal Organic Framework, and "others") is a path being explored by many R&D organisations.**

# Performance & cost targets

| | Required performance | Hydride | Alanate | 'Other' |
|---|---|---|---|---|
| **Storage Capacity** | At least 3% wt with potential for 5% wt | 1.8% | 3.6% | 3% |
| **Cycling** | 1000<br>+ *robust to gas impurities* | 1000 | ? | 1000<br>yes |
| **Operating conditions** | Up to 20 bars<br>Ambiant to 80°C | 1-20 bar<br>60°C | 1-20 bar<br>35°C | 1-20 bar<br>0 - 80°C |
| **Safety** | Non - flamable product when exposed to air | NO | NO | YES |
| **Cost** | Below 10 $ /kg | 50 ? | ? | 5 |

# Early niche applications

**Achieving a reversible storage capacity in excess of 3% wt. at a cost below 10 $/kg would open early niches where H2 storage material could prove to be competitive.**

**Electrolysers are increasingly used in stationary applications for producing high purity H2 in labs or electronics manufacturing sites. They are also considered as a source of on-board hydrogen supply for Nitrogen oxides (NOx) reduction on heavy duty diesel engines (e.g. trucks in North America).**

**A small storage buffer, containing up to 200g of H2, could be a valuable complement to provide peak shaving as well as some contingency storage for electrolysers, while operating at relatively low pressure (<20 bar).**

# Early niche applications cont'd

A **portable container** of similar specification could be used to supply small fuel cells for back-up power. A 200g container would provide some 2 kWh of electricity. The same device could be used for portable applications: - power tools, small power generator, scooter, when small fuel cells become affordable.

**Large containers** (1 – 20 kg H2) could be envisaged for storing H2 on-board trucks to reduce NOx, possibly replacing electrolysers mentioned above. Over time, as cost decrease, these containers could replace high pressure H2 cylinders (200 bar +) currently used for industrial application.

**Hydrogen filling stations** require storage of 500 – 2000kg of hydrogen. H2 storage materials could provide safer and cheaper storage in replacement of high pressure H2 cylinders  or liquid hydrogen. In the short term there is scope to retrofit 70 existing stations and equip some 10 new station every year.

# Buffer and portable containers

**A small, low pressure (<20 bar) container able to supply small quantities of hydrogen, typically: - 200g of H2 for a 5 litre size and a system weight < 10kg.**

**Buffer storage for electrolysers is an existing opportunity. Indeed electrolysers are increasingly used for producing very high purity H2 for instance, in laboratories or the electronic industry. Buffer containers based on hydrogen storage materials would provide a much higher storage capacity at low pressure compared to a compressed H2 storage.**

**Small fuel cells systems (<2kW) are beginning to be used for back-up power supply and require a H2 storage supply. Small containers for power tools or scooters will take-off only when a cost break-through is achieved on small size fuel cells. Timing of such an event is uncertain.**

**In the USA / Canada, electrolysers on-board trucks are being considered as a means to reduce NOx exhaust emissions. A small buffer is necessary to supply H2 during the engine and electrolyser start-up phase. Fitting such devices to new trucks, or retrofitting it to the existing park, could result in the annual sale of hundreds of thousands of electrolyser/buffers systems, and consequently sales of 1kT/year or more of H2 storage material.**

# Electrolysers and fuel cells

**Proton Energy - HOGEN GC**
Hydrogen generators designed for scientific applications, produce grade (99.9999+%) hydrogen at pressures up to 200 psig. Both 300 cc/min and 600 cc/min are available.

**Proton energy -HOGEN H Series**
Hydrogen generation systems produce ultra-high purity hydrogen gas with capacities from 2 Nm3/hr to 6 Nm3/hr

**From Proton Energy**
***www.protonenergy.com***


**Idatech back-up power system**
***Courtesy Idatech media kit www.idatech.com***

# Framework for NOx reduction in heavy duty diesel exhausts

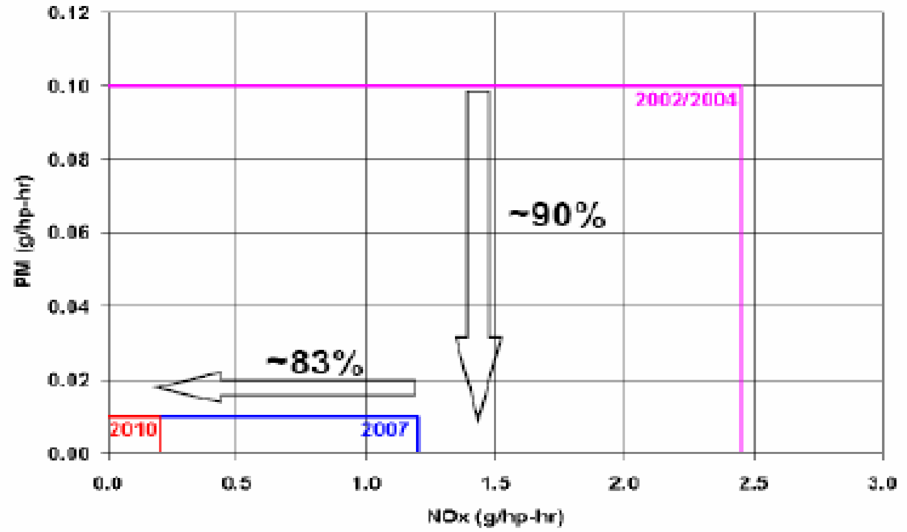
**There is an increasing level of NOx and particle reduction stipulated by the EPA for US heavy diesel applications up to 2012. The most aggressive NOx reduction is from 2007 to 2010. The USA is following a different strategy to Europe for NOx reduction.**

**Europe is using urea systems which would achieve US targets.**

**In the USA, the EPA wants 'user invisible' technology without a separate 'fuel' and a guarantee that the system is in use.**

**Further issues exist on the cost of infrastructure for a urea SCR system.**

**The 2007 NOx limit is achievable – no technology, other than urea SCR, has been proven in large scale tests to satisfy the 2010 targets.**




*Note: Urea produces ammonia which in turn reduces the NOx. Specific infrastructure and large catalyst volumes are required.*

# USA - NOx reduction initiatives

**There have been many NOx reduction initiatives in the US, including:**

- **Recirculation of exhaust gases**
- **Changes in engine timing to reduce NOx production at source**
- **Introduction of hydrogen into the cylinders**
- **NOx traps, with intermittent regeneration**
- **Various forms of selective catalytic reduction including $NH_3$, HC (lean burn), HC+$H_2$ over precious / transition metal catalysts**
- **Plasma processes**

**2007 NOx limit could be met by engine timing adjustment and introduction of $H_2$ into cylinders, at the expense of fuel efficiency.**

**Selective Catalyst Reduction using $H_2$ is being considered for meeting 2010 target.**

# On-board electrolysers for heavy duty engines

**Since 1996 the Canadian Hydrogen Energy Company Ltd. (CHEC) and its founders have been working towards bringing hydrogen based technologies to market. In 2004 CHEC launched the Hydrogen Fuel Injection System, ready for the commercial trucking industry.**

**The CHEC HFI system works as follows:**

**Hydrogen Fuel Injection System (HFI), is an onboard generator of hydrogen and oxygen gases for internal combustion engine. The HFI system introduces gases to the air intake manifold of the truck, weighs approximately 40kg and measures 30x30x60cm.**

**The gases generated, once introduced to the intake manifold, are mixed with the incoming air. The gases are produced only while the engine is running.**

**Hydrogen is not stored under significant pressure at anytime eliminating any safety concerns. The introduction of these gases results in a more efficient and complete burn of existing fuel.**

# HFI system

***(from www.chechfi.ca)***

- Hydrogen is carried to air intake
- Produces a nearly complete combustion at the top of the piston stroke
- Engine efficiency and power improved
- Engine wear and emissions reduced

No Hydrogen stored means safe, hassle-free operation


- Hydrogen is produced on demand during operation.
- Requires only about 4 litres of distilled water per 10,000 kilometers.
- Uses only about 15 amps of electricity to operate (about the same as your headlights)
- Stainless steel enclosure protects and looks great
- Attaches at any convenient location


Confidential © iti Scotland Ltd

# Large containers

**For truck NOx reduction, an alternative to electrolysers could be on-board storage of H2 using a container sufficiently large to last 2000 km, before refilling or exchange.**

**To meet this requirement, about 2kg of H2 would be needed, which could be supplied from a storage container of 50 litre and total weight of 100 kg.**

**Fitting such devices to new trucks, or retrofitting it to the existing park, could result in the annual sale of hundreds of thousands of containers, and consequently sales of H2 storage material in excess of 10 kT /year.**

**Over the long term, H2 storage material could become competitive for the H2 bottle market. To do so, it would need to reach a storage capacity close to 4% and be made available at a price below 5 $/kg.**

**In the USA, annual sales in the hydrogen cylinder market are close to $500 million, corresponding to H2 volumes of 200 – 300 kT/yr.**

**Replacing these cylinders over a period of 10 years would require an annual production of 20 kT/yr of H2 storage materials, worth 100 M$/yr.**

# Large container – case example

EC FP 5 Programme 1998-2002

## HYSTORY

Institute for energy technology
Stockholms universitet
CNRS Centre National de la Recherche Scientifique
Environmental Research Laboratory
TREIBACHER Innovation is our tradition.
Société Commerciale de Métaux et Minerais
Statkraft
ABB
KOCKUMS

### Glashusett - Stockholm

Current hydrogen storage unit in GlashusEtt: Conventional $H_2$ storage consisting of 22 bottles, each with a water volume of 50 litres, giving a total volume of 1100 litres. At 14 barg this storage contains 15 Nm³ of $H_2$.

Large scale metal hydride tank designed to store 15 Nm³ of $H_2$. The outer volume of the tank is approximately 90 litres. This tank is shortly to be installed in GlashusEtt.

ENK6-CT-2002-00600: Hydrogen Storage in Hydrides for Safe Energy Systems

**To store 1.3 kg of hydrogen, a 90 litre tank containing metal hydride replaces 22 bottles of 50 litres (1100 litre) at 14 bar.**

**(Tank made by Treibacher www.treibacher.com)**

**Hystory is a European Project, visit http://milos.ipta.demokritos.gr/hystory/**

# Hydrogen filling stations

**There is potentially a relatively large development market for hydrogen refuelling stations, both for refurbishing the existing stations or building new ones. Of course this depends on how quickly hydrogen moves into the transport sector.**

**Moving to H2 on-board storage for truck NOx reduction could justify building hydrogen dispensers in an increasing number of service stations. In the world, there are currently about 70 hydrogen refuelling stations and about 10/year are built *(ref Worldwide Hydrogen Fueling Stations, by Fuel Cells 2000).***

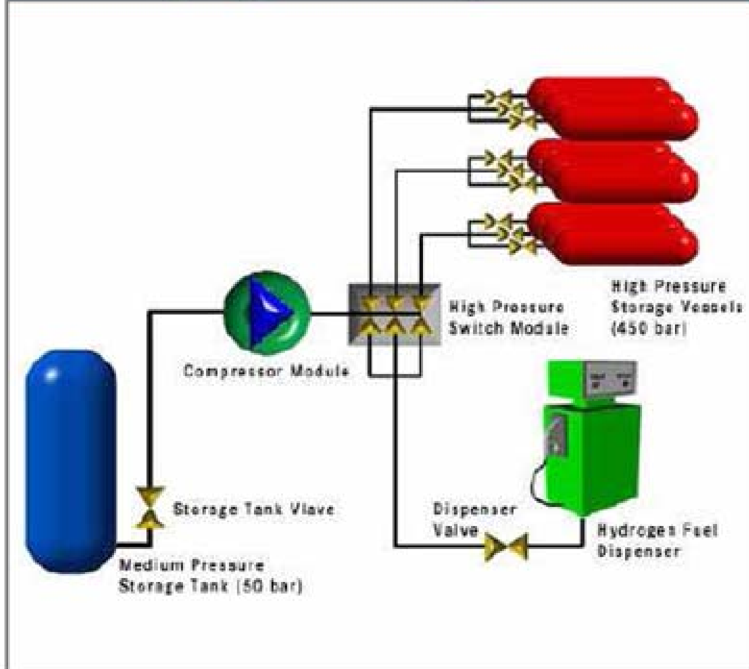
**A typical station would need a buffer storage of 0.5 to 2 tons of H2, and thus could have an inventory of up to 100 tons of storage material. The use of H2 storage material for this buffer at a relatively low pressure would considerably enhance the safety case for H2 stations, especially in relation to regulatory distances.**

**The cost of the H2 storage material would be a significant part of the filling station investment. It should definitely be below 10 $/kg, and preferably < 5 $/kg.**

# Filling station - schematics

**Hydrogen vehicles will require refuelling infrastructure, including storage between deliveries or as a buffer for local production.**

**Schematic of conventional hydrogen refuelling station**




Source: http://www.fuel-cell-bus-club.com

**Comments**

- To fill the tanks of fuel cell vehicles a hydrogen filling station with a compressor is required. A typical hydrogen station is quite similar to a natural gas filling station
- **Medium pressure storage tank:** In case of a central delivery by road transport this tank stores the hydrogen to fuel the buses for several days. In case of on site production this tank will be fairly small and acts as a small buffer storage between the hydrogen production equipment (electrolyser, steam reformer) and the compressor
- **High pressure storage vessels:** These vessels contain the hydrogen at high pressure. During the refuelling process these vessels will be connected to the vehicle tanks through the dispenser hose. Due to the higher pressure in the storage tanks as compared to the vehicle tanks the hydrogen will automatically flow into the bus tanks until these tanks are properly filled

H2 storage material allows large quantities to be safely stored under medium pressure storage

# Various hydrogen filling stations

(Photography courtesy Shell Hydrogen, picture gallery)

Hydrogen filling station for buses - Luxembourg


H2 dispenser in Shell station - Washington


Re-filling an H2 bus Amsterdam

# Conclusion

**This study has highlighted a number of niches which can be captured by H2 storage materials as they become more competitive.**

- **an existing small niche as a complement for electrolysers**
- **a speculative application for NOx reduction in exhausts of heavy duty diesel engines for trucks, potentially worth more than $50million in annual sales. This could be a stepping stone towards setting-up an H2 dispensing infrastructure in service stations**
- **a small niche in current and new H2 station, with growth potential from a few $million to more than $50million in annual sales over the long term**
- **as costs decline, the potential to enter the established H2 cylinder, through a paradigm shift, and access a market segment worth more than $100million in annual sales**

**There may be a few others that ITI members might wish to bring to our attention!**

# Niche opportunities