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Hydrogen Storage Technologies Performance Overview

Does a 6% gravimetric density storage system really have more hydrogen per kg than 2%?

(the information in this document is based on public information and experts' opinion)

Contents

Scope

This document

- Points out some common misleading performance presentations
- Compares various hydrogen storage technologies

Since it is commonly established that compressed hydrogen is excessively costly and requires substantial safety measures, this document will not deal with this technology.

Comparison charts can be found at the end of this document.

General

Hydrogen storage is a “hot” issue.

The only mature technology is highly compressed hydrogen that is too expensive to be fossil fuels replacement.

Intensive basic and applied research has been performed over the last years for storing hydrogen in chemical compounds.

The w/w of hydrogen that can be stored in a given chemical compound ("gravimetric density") is regularly presented as the prime criterion. **This is not the official definition, and may lead to wrong conclusions, design failure and unacceptable operational costs.**

For systems' evaluation, a 5kg hydrogen storage and release system will be taken.

Toyota Mirai's storage tank weight 87.5kg for 5 kg of hydrogen - 5.4%. To be used by the fuel cell, the system needs high pressure tanks, valves, sensors and regulators – reducing the overall hydrogen storage density to about 5%, **raising cost and having safety issues.**

A hydrogen storage material that contains **6% w/w** of hydrogen may need a dehydrogenation unit that weighs 250 kg (due to high enthalpy of reaction - high temperature or pressure requirements). Therefore, for 5-kg hydrogen the actual hydrogen storage density in this system is **1.5%**!

Conversely, a storage system containing only **2%** w/w of hydrogen in the chemical carrier, but with a dehydrogenation unit that weighs only 40 kg (due to a very low enthalpy of reaction, and near ambient temperature and pressure required for hydrogen release) encompasses hydrogen weight fraction of **1.7%, more than the value of the "6%" system.**

There are additional parameters, crucial for the system cost effective operation:

Temperature and pressure. High values may be prohibitive for on-board application (DOE requires temperature under 100°C) and may request very heavy and expensive equipment.

Operation cost. Sodium borohydride contains **10.6%%** w/w hydrogen (as solid, and only 4.5% in the solution of a real system). Chrysler developed the Natrium car with this compound, but the **program has been cancelled due to unacceptable operational costs.**

Process details. In some cases, the hydrogenated and dehydrogenated compounds are both liquid and their separation is not straightforward. This means a real diminution in the efficacy of storage and transportation, as some of the hydrogen carrier material cannot be used in the dehydrogenation reactor.

Misleading data presentation

1. Gravimetric Density

Several companies announce gravimetric density as the hydrogen weight percentage in the carrier molecule, which is not relevant to most applications.

Gravimetric density is defined as the weight ratio of used hydrogen to the entire system weight.
DOE publication (https://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage_explanation.pdf page 9) states the gravimetric density targets for light vehicles:

"Useable specific energy from H2 (net useful energy/max system mass)" "Targets are for a complete system, including tank, material, valves, regulators, piping, mounting, brackets, insulation, added cooling capacity, and or balance-of-plant components").

For example: The Dibenzyltoluene – Perhydrodibenzyltoluene reaction cycle
The later material is the hydrogen carrier ($C_{21}H_{38}$). 9 molecules of hydrogen can be theoretically released (in a real system only 80% are released as explained below, and as stated in technology provider's publication). The theoretical chemical percentage of hydrogen is therefore 9x2/(21x12+38x1) = **6.2%.**

Based on this value, 80 kg of carrier liquid is required for generation of 5 kg of hydrogen.

However, the discharge process requires 350 °C and pressure of 5bar, which necessitates a robust and heavy reactor. Assuming reactor, pumps, pipes, and heating unit weight is 250kg, the real hydrogen storage density for 5 kg hydrogen system is only 5/(80+250) = **1.5%**

The real situation is inferior. Both materials are miscible liquids that cannot be easily separated and therefore only about 80% of the liquid is used in the dehydrogenation reactor. Thus, a more realistic value is about **1.2%.**

For comparison, let us consider the Formate – Bicarbonate storage system. The hydrogen density is only 2%, therefore 50 kg of liquid is required to carry 1 kg of hydrogen.
Due to dehydrogenation reaction conditions - working at near ambient temperature with no pressure, the reactor and its peripheral equipment weight is only 40kg. Therefore, the genuine gravimetric density is 5/(250+40) = **1.7%.**

Summary
A "6%" system has only 1.2% real hydrogen gravimetric density
A "2%" system has 1.7% real hydrogen gravimetric density

2. Required process energy

There are two types of energy inputs involved in a chemical storage system:
- Chemical reaction energy (enthalpy of reaction)
- Energy for heating/cooling and pressurizing

Publications usually mention the first one only. But this can be MUCH less than the real energy consumption.

Example: Dibenzyltoluene (DBT) – Perhydrodibenzyltoluene (PerhydroDBT)

Publications state 71 kJ/kg of hydrogen required for the dehydrogenation process. It is also stated that 350 °C and 5b are required. The reaction is carried out in gaseous phase; therefore, there is an obvious need of heating and then evaporating energy.
1 kg of hydrogen means 16 kg of carrier liquid that needs about 11 kWh/kg of energy for heating and evaporation, which is about 40,000 kJ/kg and not 71kJ/kg!.

3. Significance

The above discussion has a serious impact on application economics.

Assume an industrial plant or a commercial center that consumes 1 MW of electricity with 0.1$/kWh tariff. Annual one year hydrogen consumption is 584,000 kg of hydrogen.
A high temperature and high-pressure system requires at least 20 kWh/kg of hydrogen.
A system that works in near ambient conditions will need about 2 kWh/kg of hydrogen.
The difference is around $1,000,000 per year.
One thousand of such consumers mean **annual saving of $1B.**

Hydrogen storage technologies

Hydrogen storage technologies are divided into two main groups:

- Physical based storage
- Compressed gas
- Cold/Cryo compressed
- Liquid H_2
- Absorbents

- Material based storage
- Liquid organic (LOHC)
- Metal hydride

- Ammonia

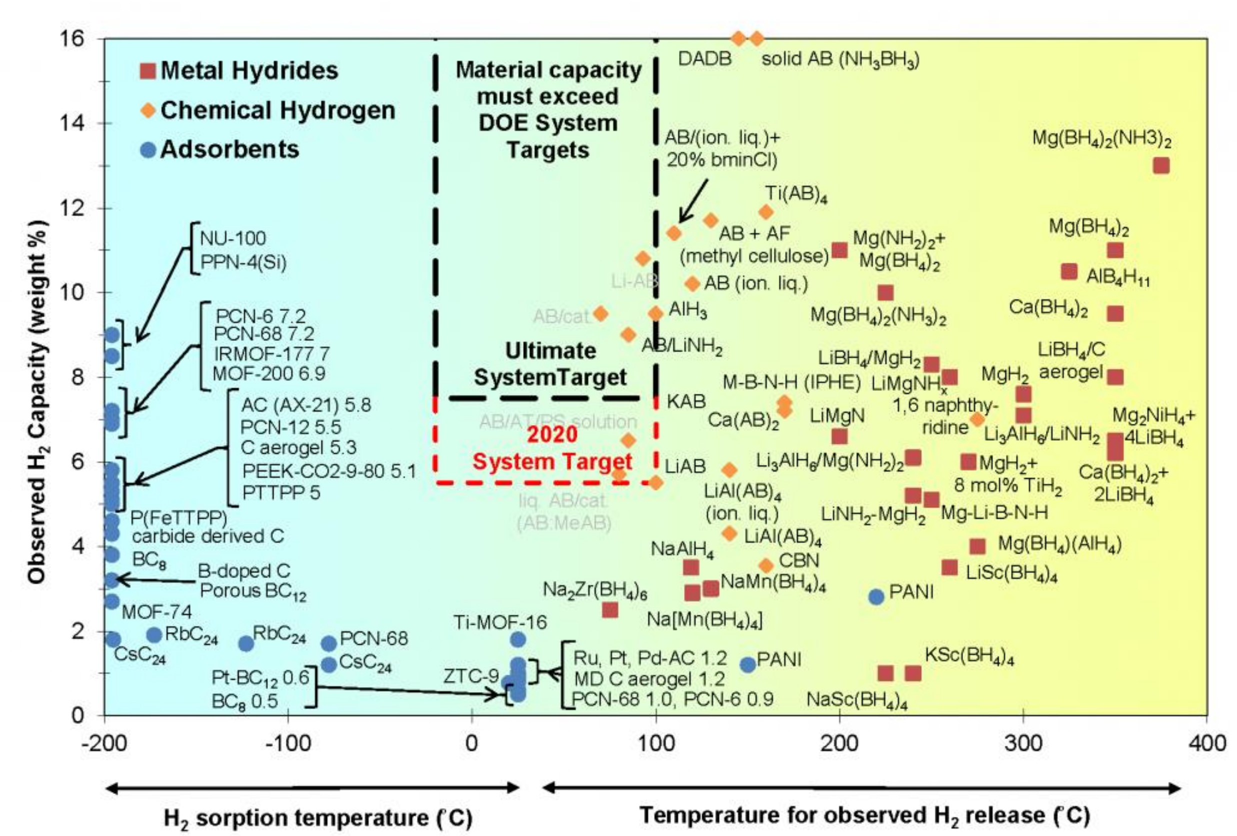
In this document, we do not analyze the physical based storage, as it is commonly agreed that high-pressure systems are too expensive and need serious safety measures.

The figure below shows hydrogen gravimetric capacity as a function of hydrogen release temperature for many of the unique hydrogen storage materials investigated by FCTO (https://energy.gov/eere/fuelcells/materials-based-hydrogen-storage). It can be seen that all storage materials call for high operation temperature, more than required by the DOE.

Moreover**, high temperature means:**

1. **High energy consumption**
2. **High volume and weight reactors**
3. **Long start up time, till operating temperature is achieved**

In many cases, high pressure is also required.



Liquid Organic (LOHC)

Unsaturated organic compounds can store high amounts of hydrogen. These *Liquid Organic Hydrogen Carriers* (LOHC) are hydrogenated for storage and dehydrogenated, when the energy/hydrogen is needed.

The major disadvantage of most of LOHC materials is the need for high temperature and/or pressure for hydrogenation and/or dehydrogenation. This means **too high cost or system volume**.

<u>Toxicity of LOHC</u>

Most of the LOHC compounds in use/research today <u>are not fully characterized</u> for their potential toxicity and hazards. Companies developing LOHC-based storage systems are claiming for “safety” without enough proved data, much more research must be done to prove the safety of LOHC.

The most promising LOHCs are listed and discussed below.

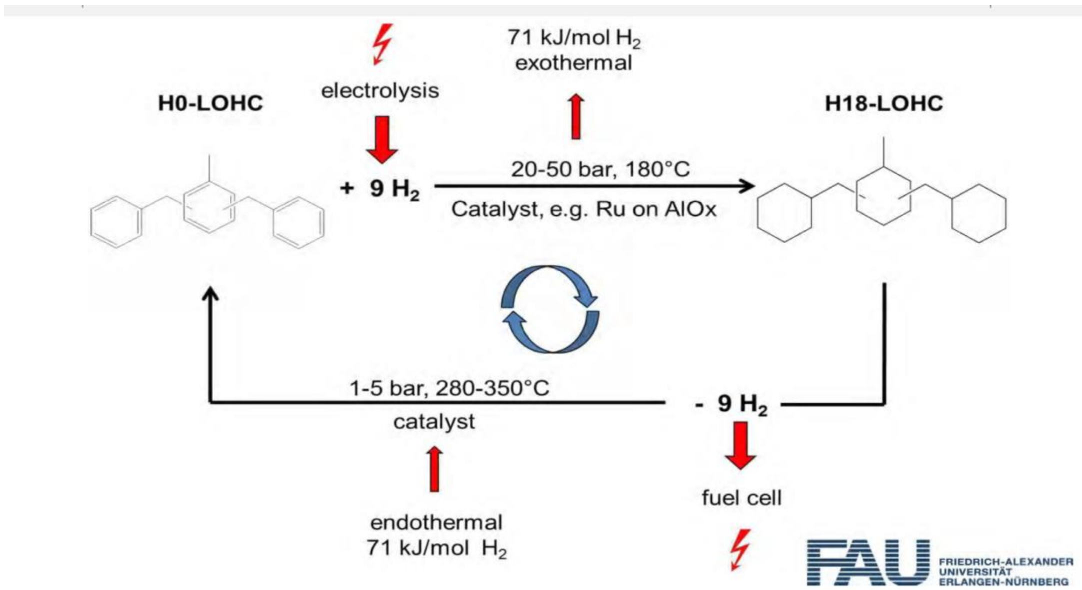
Toluene – MCH

This dehydrogenation reaction requires about **400 °C** and 10 bar, which means costly and high-volume systems.

Toluene is **toxic, carcinogenic and flammable**.

Dibenzyltoluetne – Perhydrodibenzyltoluene

Dehydrogenation requires **350°C** and 5 bar, which means costly and high volume systems



Hydrogenation reaction requires 50 bar, which needs compressors and has cost consequences.

The picture below (taken from Hydrogenious web-site) gives the impression of such a system size. Such systems may produce, after fuel cell, about 10 – 120 Kw. A personal vehicle requires 50 – 100 kW. Such a system, even after downsizing cannot serve transportation goals.

Hydrogenious ReleaseBOX

ReleaseBOX	Series 5	Series 33	Series 100
Hydrogen outlet	5 Nm³ / h	33 Nm³ / h	100 Nm³ / h
LOHC consumption	8 l / h	53 l / h	160 l / h
Container size	Rack	10 ft.	20 ft.

As the materials used in this technology are not very commonly used their safety is not well enough established. As they are quite like toluene, it can be assumed that their toxicity is very close to toluene as described in the previous paragraph.

Metal Hydrides

Metal hydrides load hydrogen in **250°C - 800°C** (most of them – **over 600°C) and** pressure between **200 bar to 300 bar.**

Dehydrogenation requires **120°C to 500°C** (most of them **above 200°C).**

One of the most promising technologies for on-Board Vehicular hydrogen Storage - **sodium borohydride (NaBH4)** was tested on Chrysler Natrium. The hydrogen gravimetric density was less than 4.5% - the 2007 DOE target.

The Independent Review Panel, Go/No-Go Recommendation for Hydrolysis of Sodium Borohydride for Onboard Vehicular hydrogen storage was "The hydrogen storage technology considered for the hydrolysis of sodium borohydride (NaBH4) has clearly not met all the 2007 targets. In addition, the Panel sees no promising path forward for this technology to reach all the 2010 targets. Based on its charter, then, the Panel unanimously recommends a No-Go decision"

(https://www.hydrogen.energy.gov/pdfs/42220.pdf).

One of the main reasons was the cost of regeneration - "In terms of hydrogen cost and energy efficiency, the Panel found the high energy penalty and cost of regenerating sodium borate (NaBO2) back to NaBH4 fuel to be of significant concern."

The high temperature and pressure required made this very promising system useless.

Same drawback makes other Metal hydrides too expensive to be a useful solution, though they may be better than highly compressed hydrogen.

The borohydride water solution has stability issues. Borohydride decomposes in presence of water and it is stabilized with NaOH which is highly corrosive and has to be handled with care. In 4% NaOH in water, used in Chrysler program,

- 0.2% hydrogen loss in a day
- 1.4% hydrogen loss in a week
- 6% hydrogen loss in a month
- 36% hydrogen loss in six months

Recently, potassium borohydride has been proposed to replace the sodium borohydride as hydrogen carrier. Both materials have very similar properties.

It is important to notice: potassium borohydride is less soluble than the sodium borohydride - 190 gr/ liter vs. 550 gr/liter, and the hydrogen density is lower – 7.4% for the potassium borohydride vs. 10.6% for the sodium borohydride (hydrogen densities are for the solid form of the salts). Operation with potassium borohydride is done in a solution. Therefore, the hydrogen density will be significantly lower in solution.

In both hydrogen loading processes (sodium borohydride and potassium borohydride) there are extreme reaction conditions and need for a third chemical entity, a metal, participating in the reaction. The recycling of this metal is expensive and the overall cost of hydrogen loading is a stumbling block.

The hydrogen discharge reaction is a solution containing borohydride and the borate. This limits the conversion, i.e. the percentage of borohydride that releases hydrogen, leaving a proportion of "unused" borohydride returning with the borate for regeneration – hydrogen loading. Therefore, more potassium borohydride should be in the container.

Stability of potassium borohydride is even worse compared to sodium borohydride.

Ammonia

Ammonia is not a rechargeable material.

The high temperature, 900°C**,** needed for hydrogen release from Ammonia is the main reason preventing this technology from being a leading hydrogen storage material. The required reactors are very large and heavy. See below DOE publication and their decision not to support this storage direction.

The production of Ammonia also needs lot of energy. It is carried out at **500°C and 300b**.

Ammonia is toxic and corrosive.

https://www.hydrogen.energy.gov/pdfs/nh3_paper.pdf

Given the state of the art in 'cracking' ammonia to produce hydrogen, there are many issues in the on-board use of ammonia similar to those identified for on-board fuel processors. Specifically, these include: high operating temperature (>500° C); longevity and reliability of catalysts and other components (at high temperatures and in the presence of impurities); start-up time (to get the system up to operating temperature); purification requirements (to prevent ammonia poisoning of fuel cells); complexity of the overall system; energy efficiency (on-board ammonia would have to be burned in the cracking process); cost (currently ~$100K for 1-3 g H_2/s stationary units); and reactor weight and volume (commercial units with sufficient throughput currently weigh about 2000-5000 kg and are about 3000-6000 liters in size). Simply stated, most of the performance parameters of ammonia reactors would need at least two orders-of-magnitude improvements in order to be used on-board commercially viable hydrogen-powered fuel cell vehicles

Ammonia with chemical content of 17.6% hydrogen needs reactors which weight over 1000 kg. The real value is less than 0.09%!

NrgStorEdge advantages and “disadvantage”

NrgStorEdge Formate-Bicarbonate system has "only" 2% Hydrogen density. This may sound as a serious drawback.

But with almost zero enthalpy of reaction and near ambient conditions for charging and discharging there is an **advantage for onboard system even in weight.**

Its release reactor and peripheral equipment is about 40 kg for car application, which means about 1.7% real density.

For comparison, Ammonia has less than 0.09%.

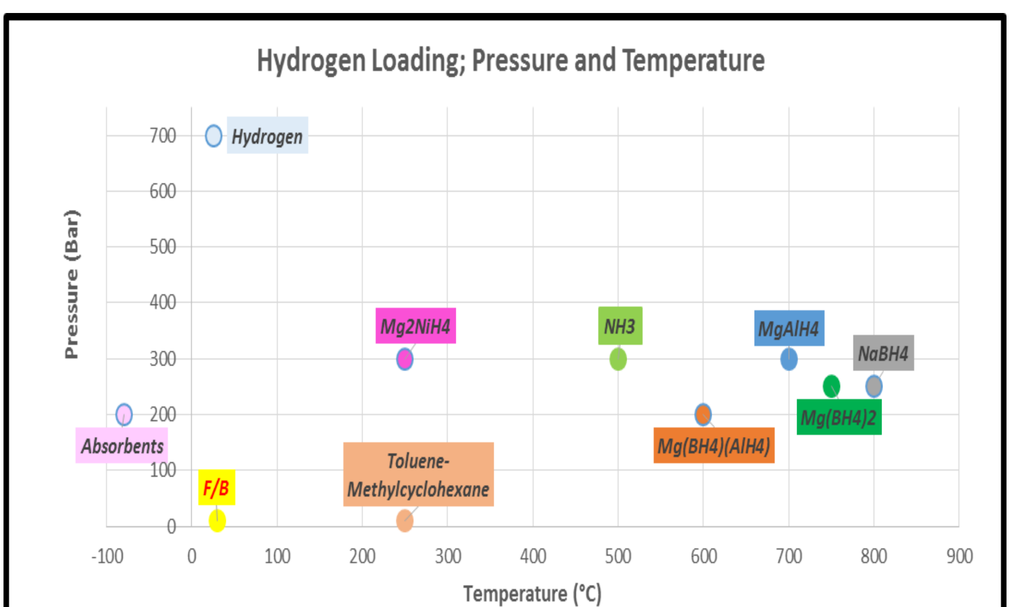
MCH about 1.5%.

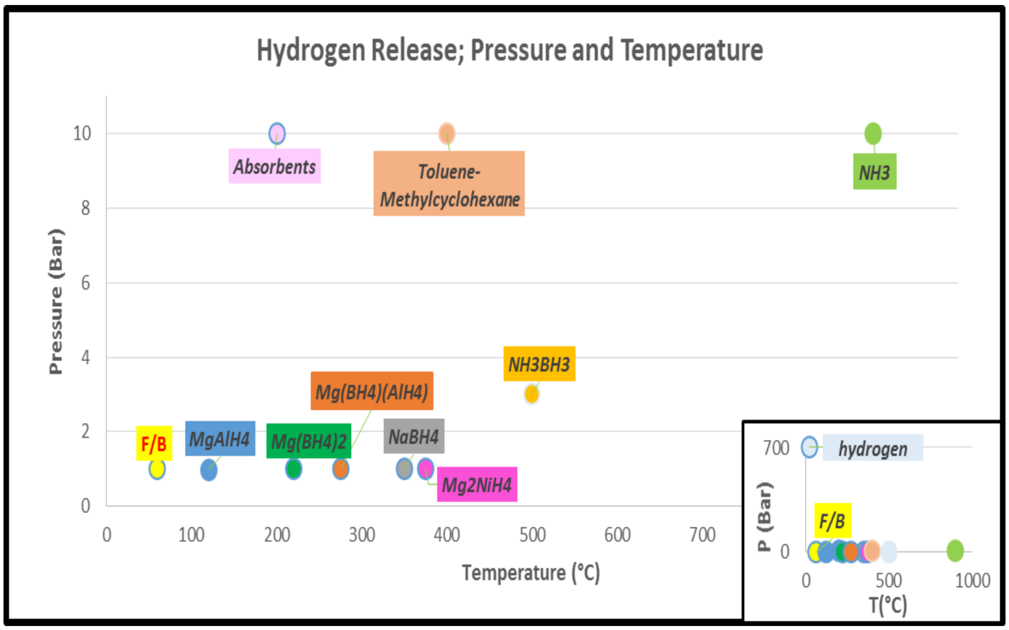
PerhydroDBT 1.4%.

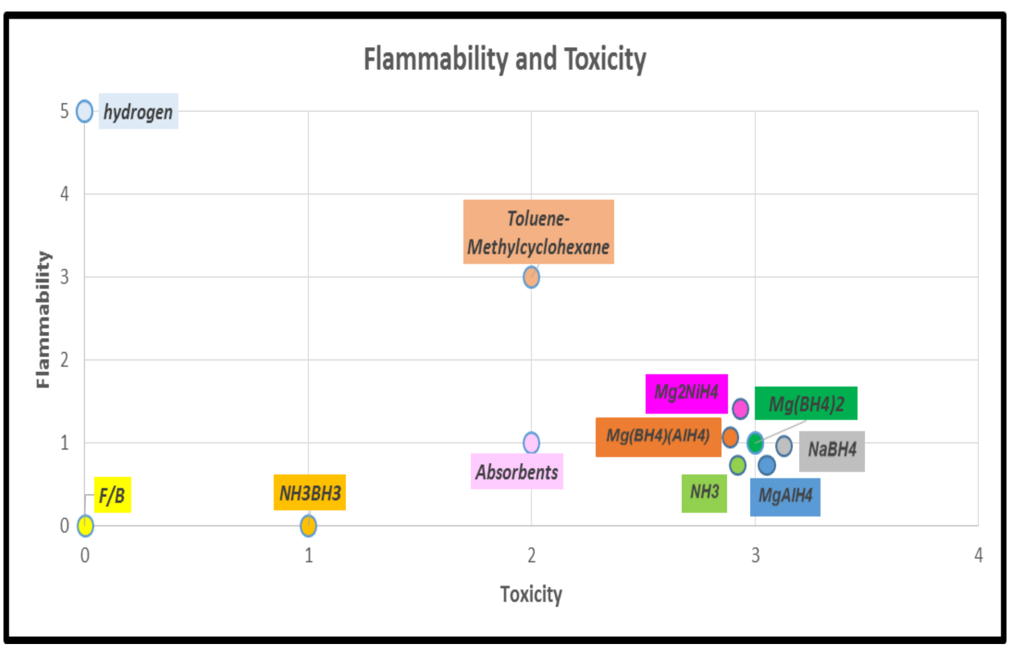
The low enthalpy and near ambient reaction conditions result in unique advantages over all other technologies:

- No start up time (no need of long time to reach high temperature and pressure)
- Small reactors
- Very low cost of equipment
- Very low cost of operation (down to 20$ for 500km driving range, **including** hydrogen cost!)
- Water-like safety

The following graphs compare NrgStorEdge (F/B = Formate/Bicarbonate) and most promising technologies. The parameters are: Loading pressure and temperature, Discharge pressure and temperature, Toxicity and Flammability and required chemical process energy.




Hydrogen Release; Pressure and Temperature
Pressure (Bar)
Temperature (°C)
Absorbents
Toluene-Methylcyclohexane
NH3
NH3BH3
Mg(BH4)(AlH4)
F/B
MgAlH4
Mg(BH4)2
NaBH4
Mg2NiH4
hydrogen
P (Bar)
T(°C)


Flammability and Toxicity
Flammability
Toxicity
hydrogen
Toluene-Methylcyclohexane
Mg2NiH4
Mg(BH4)2
Mg(BH4)(AlH4)
NaBH4
Absorbents
F/B
NH3BH3
NH3
MgAlH4