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Hydrogen from sodium borohydride and fossil source: An energetic and economical comparison

M. Monteverde*, L. Magistri

TPG-DiMSET, University of Genoa, Via Montallegro 1, 16145 Genoa, Italy

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ABSTRACT

In this paper, sodium borohydride ($NaBH_4$) is examined as a method of hydrogen storage and transport, and compared with hydrogen obtained from fossil sources. This chemical hydride has a very high storage density capability due to its large hydrogen content. Hydrogen is released as the main product of the reaction of $NaBH_4$ with water, with sodium metaborate ($NaBO_2$) as a by-product. The main disadvantage of the process is the production cost of the borohydride.

In this paper, an economic analysis is carried out of the production, storage and transport of hydrogen from $NaBH_4$ and from fossil fuels.

Finally, a comparison is presented between various vehicles fuelled by petrol, hydrogen and sodium borohydride.

1. Introduction

A possible remedy for rising pollution and carbon dioxide emissions (with the resulting increased greenhouse effect) may be to use hydrogen fuel cells to power vehicles and for distributed energy cogeneration, thereby improving the environment in which we live.

Hydrogen is not an energy source as commonly defined, but an energy carrier, i.e. a means of transporting energy. It is not only a potentially inexhaustible resource, but is also non-polluting: when used in combustion systems, it outputs only water vapour and traces of nitrogen oxides, while when used in electrochemical generators (fuel cells) it produces only water vapour.

Alongside these advantages, hydrogen has a few problems which, together with the high production cost, have so far hindered its application: it is explosive, highly flammable and extremely volatile. Thanks to recent technological advances, however, these problems can be overcome, and new production, storage and transport technologies, once mature, will make it competitive.

Hydrogen can readily be produced on an industrial scale either from fossil energy sources, such as natural gas through reforming and coal though gasification, or with electricity through the electrolysis of water. The key factors in all these processes are the cost of the energy input and the efficiency of energy conversion. Hydrogen production from biomass gasification could offer the most efficiency pathway from renewable resources. There are also other ways of producing hydrogen, such as bio-production by algae and bacteria, and high-temperature direct splitting of water in solar thermal plants.

The technology of hydrogen storage is one of the key subjects in the context of a hydrogen economy considered as a potential solution to the increasing demand for energy alternative sources to today's dwindling fossil fuel reserves. Hydrogen can be stored in gaseous form (compressed gas), or in liquid form (20 K), and also in solid media. The first two

* *Corresponding author*.
E-mail address: michela.monteverde@unige.it (M. Monteverde).

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Table 1 – DOE Technical Targets: On-Board Hydrogen Storage Systems [1].

Storage Parameter	Unit	2010	2015	Ultimate
System Gravimetric Capacity: Usable, specific-energy from H_2	kWh/kg	1.5	1.8	2.5
	(kg H_2/kg system)	(0.045)	(0.055)	(0.075)
System Volumetric Capacity: Usable energy density from H_2	kWh/L	0.9	1.3	2.3
	(kg H_2/L system)	(0.028)	(0.040)	(0.070)
Storage System Cost (& fuel cost)	$/kWh net	4	2	TBP
	($/kg H_2)	(133)	(67)	
Fuel Purity (H_2 from storage)	% H_2	99.99	(dry basis)	

methods are fairly well-established technologies with several limitations, the most important of which is their energy-intensive character. Solid-state hydrogen storage, still in its infancy, appears to be an attractive possible alternative. This is particularly due to its greater safety and volumetric energy density. However, if this solution is chosen there are penalties to be paid in terms of weight efficiencies, thermal management and up-scaling. Intensive research is ongoing to overcome the limitations of existing hydrogen storage technologies and to develop viable solutions in terms of efficiency and safety.

All of these production and storage techniques must meet the DOE Targets shown in Table 1.

In the last few years, research has been focused on new methods of hydrogen storage, among them chemical hydrides. Sodium borohydride is one of the most promising compounds because it is simple to transport, is not dangerous and has a high gravimetric and volumetric capacity, exactly 10.9% by weight or 109 g/L, complying with DOE Targets.

The aim of this paper is to compare the cost of hydrogen production, storage and transport using sodium borohydride with the cost of hydrogen produced by natural gas and stored in liquid or gaseous form.

1.1. *Hydrogen from sodium borohydride*

To produce hydrogen from sodium borohydride a simple process of hydrolysis is needed:

$$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2 \text{ (Reaction)} \quad (1)$$

This exothermic ($\Delta H < 0$) and spontaneous ($\Delta G < 0$) [1], reaction requires no energy and can operate at ambient temperature and pressure. A catalyser such as ruthenium is, however, necessary [2].

This reaction is known to be very safe, and more efficient and more easily controllable than other chemical methods of releasing hydrogen. The by-product $NaBO_2$ (sodium metaborate), commonly found in laundry detergents, is safe. Unlike phosphates, borates are not environmentally hazardous in water supplies.

Moreover it is completely inorganic (carbon and sulphur free), producing a high quality energy source without polluting emission. Theoretical and experimental studies [3] have confirmed the feasibility and simplicity of this process.

The total amount of hydrogen depends on several factors such as the $NaBH_4$ flow rate, concentration and temperature. This reaction is known to be accelerated by catalysts, acids and high temperatures. However, the addition of acid is undesirable. The conventional catalysts are metal halides ($NiCl_2$, $CoCl_2$), colloidal platinum, active carbon, Raney nickel, ruthenium supported on ion-exchange resin beads and fluorinated particles of Mg-based materials, as well as cobalt and nickel borides. Among them, Ru-based catalysts are known to be most effective for promoting H_2 generation.

The main disadvantage of this hydrogen storage technology is the high production cost of sodium borohydride.

1.2. *Sodium borohydride production: methods and costs*

Unfortunately, sodium borohydride does not exist in nature and therefore has to be synthesized. The process is quite complex and expensive for the following reasons:

1. It requires a combination of three different elements (Na + B + H) + electrons + energy;
2. Energy efficiency is the key, any process has to be optimized to minimize wasted energy;
3. The $NaBH_4$ price will always be driven by the price of primary energy.

The first option considered for producing $NaBH_4$ was electrochemical regeneration from $NaBO_2$. Several patents [4–6] have suggested the feasibility of this process with a current efficiency of about 20–25%.

Due to the high energy demand, this method could be convenient using energy produced by a renewable source or energy that would otherwise be unused and dispersed.

Anode side:

$$8NaOH \rightarrow 8Na^+ + 8OH^- \text{ (Reaction)} \quad (2)$$

$$8OH^- \rightarrow 2O_2 + 4H_2O + 8e^- \text{ (Reaction)} \quad (3)$$

Cathode side:

$$NaBO_2 + 6H_2O + 8e^- \rightarrow NaBH_4 + 8OH^- \; E^0 = -1.24\,V \text{(Reaction)} \quad (4)$$

$$8H_2O + 8e^- \rightarrow 4H_2 + 8OH^- \; E^0 = -0.83V \text{ (Reaction)} \quad (5)$$

$$8Na^+ + 8OH^- \rightarrow 8NaOH \text{ (Reaction)} \quad (6)$$

Unfortunately, Reaction 5 is thermodynamically preferred to Reaction 4. In order to produce the borate reduction, therefore, it is necessary to choose cathodic materials and operating conditions suitable for increasing the overpotential of Reaction 5.

Notwithstanding that some patents assert the possibility of direct electrochemical regeneration of sodium borohydride in