Short communication

Hydrogen storage in metal–hydrogen systems and their derivatives

U. Eberle*, G. Arnold, R. von Helmolt

General Motors/Adam Opel Fuel Cell Activities, International Technical Development Center, IPC MK-01, D-65423 Rüsselsheim, Germany

Available online 1 December 2005

Abstract

During the last years, the power densities of automotive fuel cell systems have been raised dramatically. However, a major technology improvement is still needed for the on-board fuel storage system since hydrogen exhibits a rather low volumetric energy density (regardless whether it is stored as a liquid at cryogenic temperatures or as a compressed gas). Furthermore, the cost for current hydrogen containers is far from what gasoline tanks cost. Therefore, alternatives like solid-state absorbers of hydrogen (e.g. metal hydrides or complex hydrides) are investigated for their feasibility by the car industry. These kinds of systems show very high volumetric storage densities on a materials basis. Unfortunately, the host compounds are usually quite heavy and thus possess a low gravimetric storage density. Also, the thermodynamics and kinetics of the absorption/desorption reactions and their impact on the tank design in general (and on the heat management in particular) have to be considered. Within the framework of this paper, the properties of the most promising solid-state storage systems are discussed and compared to those of the liquid and compressed gaseous hydrogen technologies.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Hydrogen; Cryogenic; High pressure; Hydrides; Energy density; Tank systems

1. Introduction

Tremendous progress has been made during recent years concerning H_2-propelled vehicles. The majority of the development effort hereby has been concentrated on the propulsion system (either comprising a fuel cell power module or an internal combustion engine) and its vehicle integration. Nowadays, a general consensus in the automotive industry has emerged that viable hydrogen storage technologies are as crucial for the introduction of H_2-powered cars as the propulsion unit itself.

From an engineer's point of view, the two main technologies competing to offer on-board storage capacities of at least 5 kg H_2 are:

(1) compressed gaseous hydrogen (CGH2, 35–70 MPa),
(2) liquid hydrogen (LH2, 20 K).

Both of these options have been implemented by the automotive industry in recent years (e.g. into the latest generation of General Motors/Opel fuel cell cars, the Hydrogen3). A general problem hereby is the rather low volumetric hydrogen storage density in both cases (already on a materials basis). That implies a shorter range of hydrogen propelled vehicles compared to conventional gasoline or diesel powered cars. The current Hydrogen3 vehicles have tank systems installed that are able to store 3.1 kg (CGH2, 70 MPa) or respectively 4.6 kg (LH2) of hydrogen. These quantities correspond to ranges of 270 km respectively 400 km (using the "New European Driving Cycle", NEDC).

A CGH2 system's major disadvantage is that the already limited volumetric density does not even increase proportionally to the operating pressure at high values (non-ideal or real gas behaviour, see Table 1). On the other hand, for LH2 storage systems, the problems of cooling-down losses during tanking at the filling station and the so-called boil-off phenomenon during parking have to be addressed. The term "boil-off" describes the fact that the cryogenic liquid stored inside the tank begins to evaporate after a certain period of parking (normally after some days) due to the heat inflow from outside into the vessel. That inflow cannot be prevented completely, even with a highly sophisticated vacuum super insulation and heat radiation shields in place. Subsequently, the gas pressure in the vessel rises to a certain maximum value and afterwards the H_2 boil-off gas has to be released by opening a valve.

Since both conventional technologies show drawbacks (as mentioned above), a variety of storage alternatives have been

---

* Corresponding author. Tel.: +49 6142 7 69506.
  E-mail address: ulrich.eberle@de.opel.com (U. Eberle).

proposed in recent years. Among them are:

(3) metal hydrides (or closely related novel hydrides) [1,2],
(4) decomposition of hydrogen-rich chemical compounds (e.g. borazane, methanol),
(5) cryoadsorption on high-surface materials (e.g. activated carbon, metal-organic frameworks [3,4]).

Each of these points represents an extensive research field in its own right. Hence, this paper will concentrate on giving a short review on recent developments in the area of novel hydrides.

2. Materials and methods

The biggest advantage of metal hydrides is their surprisingly high volumetric storage density which exceeds liquid or compressed gaseous hydrogen by far (see Table 1). For some hydrides (e.g. TiH_2 or VH_2), this density is even higher than that of liquid water at ambient conditions (6.7×10^{22} hydrogen atoms cm^{-3}).

What is the origin of this feature? Hydrogen in gaseous (70 MPa, 300 K) or liquid modification (0.1 MPa, 20 K) consists of H_2 molecules at a mean distance of about 0.45 nm respectively 0.36 nm, resulting from molecular interactions. In contrast, hydrogen in conventional metal hydrides dissociates on the host's surface. Electrons are then transferred into the conducting band of the host metal. The resulting "protons" (or more precisely "small polarons" [5]) diffuse into the bulk and can now occupy interstitial sites of the metal lattice (see Fig. 1), which results in a very dense packing. According to the empirical Westlake criterion, the minimum H−H distance for metal hydrides is just about 0.21 nm. Those compounds, where hydrogen is interstitially bound (e.g. TiH_x, ZrV_2H_x), retain their metallic character in many cases even after hydrogenation. Furthermore, the metallic phase is stable over a wide range of hydrogen concentrations. Additionally, the hydrogen remains mobile and thus interstitial hydrides show rather high diffusion coefficients even at ambient conditions (e.g. ZrV_2H_x: $D \approx 10^{-11}$ $m^2 s^{-1}$) [6,7].

In contrast to the interstitial hydrides, hydrogen may be also bound ionically respectively covalently. Depending on the nature of the bonds, these materials are hence categorized as either "salt-like" (e.g. MgH_2, LiH) or as "complex" hydrides (e.g. $NaAlH_4$, $LiBH_4$). The absorbed hydrogen here is largely immobile in both cases due to the strength of the hydrogen-host interactions. Complex hydrides have been suggested in 1996 as a novel, promising category of storage materials (by Bogdanovic and Schwickardi, Max Planck Institute for Coal Research [8]).
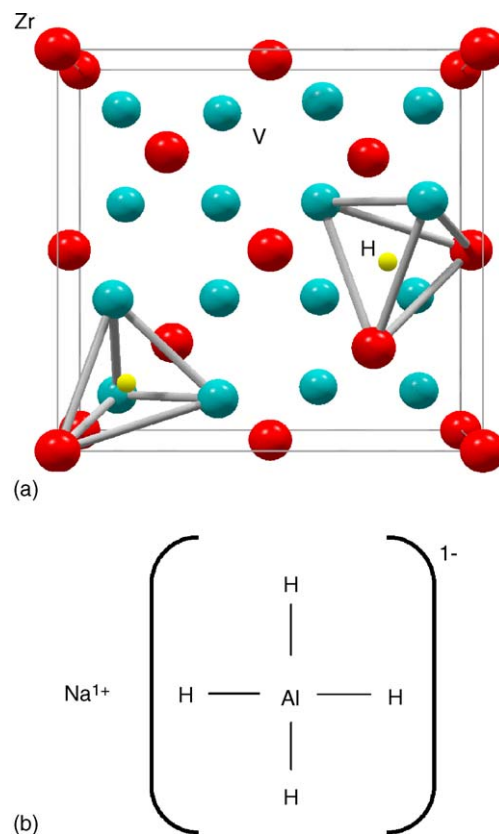

Fig. 1. (a) Interstitial hydride with two indicated tetrahedral sites (occupied by hydrogen) and (b) sodium alanate $NaAlH_4$.

From the broad range of available compounds, we now have to down-select. An ideal hydrogen absorber has to exhibit at least four main features:

(1) sufficient volumetric storage density,
(2) sufficient gravimetric storage density,
(3) favorable hydrogen absorption/desorption behaviour,
(4) cycle stability.

As mentioned above, many metal hydrides possess a high volumetric storage density. Unfortunately, the involved elements are normally quite heavy and so the number of potential candidates is reduced considerably. But the most important point is the third one: Hydrogen has to be stored safely. But equally important is the subsequent desorption and supply of the fuel to the propulsion system (see Eq. (1)):

$$M + (n/2)H_2 \leftrightarrow MH_n \qquad (1)$$

Whether hydrogen is released or absorbed is depending on the value of the Gibbs energy at the chosen reaction conditions:

$$\Delta G = \Delta H - T\Delta S \qquad (2)$$

Hydrogen is absorbed if ΔG is less than zero and consequently desorbed if ΔG is greater than zero. By switching to an appropriate temperature T, the direction of the reaction can be controlled. The change in the entropy $|\Delta S|$ between the "disordered"

Table 1
Volumetric density of hydrogen under various conditions

Compressed hydrogen (25 MPa)	1.0×10^{22} atoms cm^{-3}
Compressed hydrogen (35 MPa)	1.3×10^{22} atoms cm^{-3}
Compressed hydrogen (70 MPa)	2.3×10^{22} atoms cm^{-3}
Liquid hydrogen (20 K)	4.2×10^{22} atoms cm^{-3}
Typical metal hydride	$6–11 \times 10^{22}$ atoms cm^{-3}

Table 2
Relevant enthalpies for different hydrogen storage technologies

Storage material	Enthalpy $|\Delta H|$ (kJ mol^{-1} H$_2$)	Operating temperature (K)
H$_2$ liquid/H$_2$ gaseous	0.9	20
H$_2$ Physisorption on graphene	6–7	80
Target material (>5 system-wt.%)	<30	300
FeTiH$_x$	28	270–300
LaNi$_5$H$_x$	31	270–300
NaAlH$_4$/Na$_3$AlH$_6$	37/47	350–440
MgH$_2$	75	600

gaseous and the "ordered" bound hydrogen is always close to a range in between 100 and 130 J (K mol H$_2$)$^{-1}$.

For a hypothetical target material (10 material-wt.%) operating around ambient conditions, a reaction enthalpy of about $|\Delta H| = 30$ kJ (mol H$_2$)$^{-1}$ thus would be required. Typical values of ΔH are shown in Table 2.
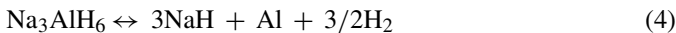
The trade-off between weight/capacity and operating conditions of hydride systems is quite problematic. Those hydrides in particular, which feature high gravimetric energy densities, release the stored gas only at temperatures around or above 600 K (e.g. MgH$_2$ and related systems). Technologically relevant systems in contrast have to offer desorption temperatures barely above room temperature (since it would be very helpful to use the waste heat of the propulsion system for heating and supplying the heat of desorption). Those intermetallic compounds, which would fulfill this criterion (e. g. LaNi$_5$H$_x$), otherwise possess gravimetric storage densities just in between 1 and 2 material-wt.%. Therefore, sodium alanate NaAlH$_4$ offers currently the best compromise between storage capacity (5.6 material-wt.%) and a favorable absorption/desorption behaviour. This complex hydride system shows the following two-step reaction mechanism [8]:

Step I:

$$3NaAlH_4 \leftrightarrow Na_3AlH_6 + 2Al + 3H_2 \qquad (3)$$
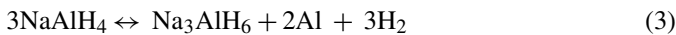
$\Delta H = 37$ kJ (mol H$_2$)$^{-1}$, gravimetric hydrogen yield: 3.7 material-wt.%

Step II:

$$Na_3AlH_6 \leftrightarrow 3NaH + Al + 3/2H_2 \qquad (4)$$

$\Delta H = 47$ kJ (mol H$_2$)$^{-1}$, gravimetric hydrogen yield: 1.9 material-wt.%

Fig. 2. Schematic drawing of a planetary ball mill [10,11]. Typical value: 500 rpm.

Complete reaction:

$$3NaAlH_4 \leftrightarrow 3NaH + 3Al + 9/2H_2 \qquad (5)$$
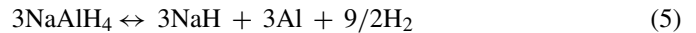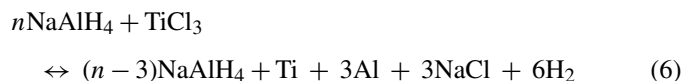
Total gravimetric hydrogen yield: 5.6 material-wt.%

The reaction is catalyzed by addition of titanium containing compounds. Either through using a wet chemical approach with Ti(OC$_4$H$_9$)$_4$ or by introducing TiCl$_3$ into the alanate material by ball milling [8–10]. The activation energy is lowered to 80 (100) kJ (mol H$_2$)$^{-1}$ for NaAlH$_4$ (NaAl$_3$H$_6$) from 120 kJ (mol H$_2$)$^{-1}$ by adding even a small amount of TiCl$_3$ (<1 mol%), but remains constant when the doping level is increased further on (see Table 3).

Ball milling (see Fig. 2) is currently the standard technology to introduce the catalyst. It is a simple, but reliable method, which is usually used for mechanical alloying purposes or to create fine powders (even nanostructures can be produced) with a lot of fresh surface [10,11]. The second effect alone already enhances the kinetics of hydrogen desorption in many compounds. However, in the case of NaAlH$_4$, the introduction of the catalyst is necessary to reach sufficient kinetics of the sorption/desorption process. Unfortunately, the storage capacity of the resulting catalyzed alanate is not only reduced by the additional weight of the dopant TiCl$_3$. While ball milling, the following reaction takes place [9]:

$$nNaAlH_4 + TiCl_3$$
$$\leftrightarrow (n - 3)NaAlH_4 + Ti + 3Al + 3NaCl + 6H_2 \qquad (6)$$

Table 3
H$_2$ desorption properties of Ti-catalyzed alanate with rate $= k \exp(-Q/RT)$, according to [9]

TiCl$_3$ level (mol%)	Constant k NaAlH$_4$ (Na$_3$AlH$_6$) (wt.% h^{-1})	Activation energy, Q, NaAlH$_4$ (Na$_3$AlH$_6$) (kJ (mol H$_2$)$^{-1}$)	Rate, R at 125 °C, NaAlH$_4$ (Na$_3$AlH$_6$) (wt.% h^{-1})	Hydrogen capacity (material-wt.%)
0	2.0×10^{13} (1.4×10^{13})	118.1 (120.7)	0.0 (0.00)	5.1
1	2.1×10^{9} (1.5×10^{11})	72.8 (97.1)	0.6 (0.03)	4.9
2	7.2×10^{10} (5.3×10^{11})	79.5 (97.1)	2.6 (0.10)	4.3
4	1.8×10^{11} ($\approx 1.0 \times 10^{12}$)	80.0 (97.5)	5.7 (≈ 0.15)	3.9
6	1.6×10^{11} (1.85×10^{12})	78.5 (98.2)	8.0 (0.24)	2.9
9	–	–	≈ 23 (≈ 0.8)	2.1

As it is shown in Eq. (6), the catalyst (zero-valent Ti) is produced by decomposing of some $NaAlH_4$. Furthermore, inert compounds (materials without a hydrogen storage capacity) such as Al and NaCl are formed. Hence, there is a critical competition between storage capacity and kinetics (which gets better, the more Ti is used). Only $TiCl_3$ levels in between 2 and 4 mol% may therefore be considered to be appropriate for H_2 storage applications (see Table 3).

During the ball milling process, the amount of H_2 released can be directly monitored [12] and thus information about the status and mechanism of the doping procedure gets accessible. Additionally, Bogdanovic et al. claim that the Ti particles are not incorporated into the alanate structure. In contrast, they would be finely dispersed in a mixed titanium/aluminum phase [13]. But this issue is still subject to an open discussion among the scientific community.

A more advanced Ti-based catalyst precursor material is $Ti \times 0.5THF$, which was synthesized by the group of Bönnemann in 1996 [14]. Hereby, the catalyst consists of colloidal zero-valent Ti nanoparticles that are coordinated to intact THF ligands. Thirteen Ti atoms form a regular cluster with six oxygen atoms (from THF molecules) in an octahedral configuration. The Ti–Ti distance in the cluster (2.83 Å) is slightly less than in hcp-Ti. The Ti–O distance was found to be 1.96 Å, which corresponds very well to the value for TiO_2.

Some years later, the nano-Ti clusters were utilized for the catalysis of the H_2 storage processes by Bogdanovic et al. for the first time. The novel catalytic compound is introduced into the alanate material by again using a ball milling procedure [15]. Compared to the conventional catalyst precursor $Ti(OC_4H_9)_4$, the hydrogenation times are shortened by a factor >40. At about 130 bar and 100 °C, the hydrogenation takes now about 10 min compared to ca. 9 h previously (in both cases 2 mol% of dopants are used). Using the nano-clusters, the H_2 capacity remains at 4.5 material-wt.% even after 25 cycles of hydrogenation and dehydrogenation (initial value: 5.2 material-wt.%). Some time ago, these results have been independently confirmed by Fichtner et al. [16]. Unfortunately, the time required for a complete hydrogenation increases again to about 2 h after 25 cycles. The cause of that degradation remains to be clarified.

Alternatively, Ti-doped $NaAlH_4$ may be synthesized directly by ball milling of a mixture of aluminum, sodium hydride and the catalyst precursor with subsequent hydrogenation [12,17].

3. Discussion and conclusions

Despite the tremendous progress in the development of catalysts to improve kinetics, some challenges lie still ahead before hydride systems may be implemented in an automotive environment: e.g. the reaction enthalpy for the sodium alanate decomposition is, as mentioned earlier, about 37 respectively 47 kJ (mol $H_2)^{-1}$ for the first and second decomposition step (see Table 2 and Eq. (2)) [18].

The appropriate operating conditions of the storage system are now given through the van't Hoff equation:

$$\ln P = \Delta H/RT - \Delta S/R \qquad (7)$$

Table 4
Typical system storage densities for various technologies

Storage technology	System gravimetric energy density (MJ kg^{-1})	System volumetric energy density (MJ l^{-1})
Diesel	33	30
Hydrides	2–4	3.5
CGH2 (steel vessel)	1–3	1–2
CGH2 (70 MPa, carbon composite vessel)	5	2–4
LH2	>6	>4
DoE target 2010	7	5.5
DoE target 2015	11	9.5

Hence, if an alanate storage system (using both reaction steps) should be utilized at an operating pressure P of several bars, temperatures $T > 100$ °C are required. Additionally, for a refilling time faster than 5 min (a time limit resulting from customer demands) of a 5 kg H_2 tank, pressures of more than 100 bar and a large heat exchanger (>300 kW) are needed.

The material storage densities of a storage compound are very important, but there are other decisive factors as well: i.e. diffusion and kinetics, de-/absorption heat, thermal and powder properties, as well as the H_2 induced volume expansion/shrinking behaviour. All these values determine a certain system design consisting of, e.g. a pressure vessel, a thermal insulation, a heat exchanger and maybe a heat-conducting matrix inside. The weight and volume of those components reduce the hydrogen storage density on a system base dramatically. Therefore, it is misleading and does not make sense to compare the system values of LH2 or CGH2 tanks with the material-based value for a hydride storage system. For a fair assessment among the available storage technologies, only the system-based numbers count. Also the new target values provided by the US Department of Energy (DoE), in the framework of the Grand Challenge Program 2003, are system values (see Table 4).

As it is shown in Table 4, hydrides are at the moment not yet mature enough for an automotive application. But considering the recent huge progress in catalyst development and the discovery of novel compounds (e.g. the Li−N−H and the B−N−H systems [19–21]) and new concepts (e.g. the destabilization of the hydride state through alloy formation [22] or low-temperature physisorption approaches) that could be used for hydrogen storage purposes, there is a fair chance to develop solid-state storage tanks, which will fulfill the ambitious, internal GM criteria and those of the Department of Energy [23].

References

[1] G. Alefeld, J. Völkl, H. Wipf (Eds.), Hydrogen in Metals, vols. 1–3, Springer-Verlag, Berlin, 1978–1997.

[2] L. Schlapbach (Ed.), Hydrogen in Intermetallic Compounds, vols. 1/2, Springer-Verlag, Berlin, 1988–1992.

[3] N. Rosi, M. Eddaoudi, D. Vodak, J. Eckert, M. O'Keeffe, O.M. Yaghi, Science 300 (2003) 1127.

[4] J.L.C. Rowsell, A.R. Millward, K.S. Park, O.M. Yaghi, J. Am. Chem. Soc. 126 (18) (2004) 5666.

[5] A. Seeger, Appl. Phys. 7 (1975) 85.

[6] A.V. Skripov, in: D. Fisher (Ed.), Defects and Diffusion Forum, vols. 224/225, 2004, p. 75.

[7] U. Eberle, G. Majer, A.V. Skripov, V.N. Kozhanov, J. Phys.: Condens. Matter 14 (2) (2002) 153–164.

[8] B. Bogdanovic, M. Schwickardi, J. Alloys Compd. 253/254 (1997) 1.

[9] G. Sandrock, K. Gross, G. Thomas, J. Alloys Compd. 339 (2002) 299–308.

[10] Schematic Drawing provided by Max Planck Institute for Metals Research (Majer Group).

[11] G. Majer, U. Eberle, F. Kimmerle, E. Stanik, S. Orimo, Phys. B 328 (2003) 81–89.

[12] J.M. Bellosta von Colbe, B. Bogdanovic, M. Felderhoff, A. Pommerin, F. Schüth, J. Alloys Compd. 370 (1–2) (2004) 104–109.

[13] C. Weidenthaler, A. Pommerin, M. Felderhoff, B. Bogdanovic, F. Schüth, Phys. Chem. Chem. Phys. 5 (22) (2003) 5149.

[14] R. Franke, J. Rothe, J. Pollmann, J. Hormes, H. Bönnemann, W. Brijoux, T. Hindenburg, J. Am. Chem. Soc. 118 (48) (1996) 12090.

[15] B. Bogdanovic, M. Felderhoff, S. Kaskel, A. Pommerin, K. Schlichte, F. Schüth, Adv. Mater. 15 (12) (2003) 1012–1015.

[16] M. Fichtner, O. Fuhr, O. Kircher, J. Rothe, Nanotechnology 14 (7) (2003) 778.

[17] B. Bogdanovic, M. Schwickardi, Appl. Phys. A 72 (2001) 221.

[18] B. Bogdanovic, R.A. Brand, A. Marjanovic, M. Schwickardi, J. Tölle, J. Alloys Compd. 302 (2000) 36.

[19] P. Chen, Z. Xiong, J. Luo, J. Lin, KL. Tan, Nature 420 (2002) 302.

[20] P. Chen, Z. Xiong, J. Luo, J. Lin, KL. Tan, J. Phys. Chem. B 107 (39) (2003) 10967.

[21] F. Baitalow, J. Baumann, G. Wolf, K. Jaenicke-Rößler, G. Leitner, Thermochim. Acta 391 (2002) 159–168.

[22] J.J. Vajo, F. Mertens, C.C. Ahn, R.C. Bowman Jr., B. Fultz, J. Phys. Chem. B 108 (37) (2004) 13977–13983.

[23] Grand Challenge for Basic and Applied Research in Hydrogen Storage, 2003 (http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/1_milliken_final.pdf).