



REVIEW

Hydrogen storage in complex metal hydrides

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Abstract: Complex metal hydrides such as sodium aluminohydride (NaAlH_4) and sodium borohydride (NaBH_4) are solid-state hydrogen-storage materials with high hydrogen capacities. They can be used in combination with fuel cells as a hydrogen source thus enabling longer operation times compared with classical metal hydrides. The most important point for a wide application of these materials is the reversibility under moderate technical conditions. At present, only NaAlH_4 has favourable thermodynamic properties and can be employed as a thermally reversible means of hydrogen storage. By contrast, NaBH_4 is a typical non-reversible complex metal hydride; it reacts with water to produce hydrogen.

Keywords: complex hydrides; sodium alanate; sodium aluminohydride; sodium borohydride; hydrogen storage.

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1. INTRODUCTION

The proton exchange membrane fuel cell (PEMFC) is currently one of the most promising alternatives to internal-combustion engines on the way to zero-emission vehicles. Probably, the most crucial problem in the large-scale application of fuel cells for mobile applications is the onboard storage of hydrogen. Apart from the classical techniques, cryostorage in liquid form at $-254\text{ }^{\circ}\text{C}$ or gaseous storage under high pressure (desirable pressure: 70 MPa), chemical storage in solid-state absorbers is a well-investigated alternative. The most promising systems are the hydride complexes of borane ($\text{M}(\text{BH}_4)_n$) and alane ($\text{M}(\text{AlH}_4)_n$). The advantages of these so-called complex metal hydrides (also known as complex chemical hydrides) are their high storage capacities and rather mild decomposition temperatures and pressures.¹⁻⁷

The storage of hydrogen can be irreversible or reversible. Irreversible storage materials liberate the hydrogen by thermolysis or hydrolysis. Irreversible storage is problematic for mobile applications since the whole storage material must be exchanged for refuelling. By contrast, reversible storage materials can be refuelled with pressurized hydrogen. To comply with this requirement, these latter materials need to have an equilibrium pressure of around 0.1 MPa at ambient temperature and at least 0.5 MPa at $90\text{ }^{\circ}\text{C}$, which is the operating temperature of PEMFCs (targets set by the Department of Energy (DOE), USA). This restricts the flexibility of enthalpy changes for reversible storage materials. The entropy of the dehydrogenation reaction is dominated by that of gaseous hydrogen ($\approx 40\text{ kJ mol}^{-1}$), so the decomposition enthalpy of the material needs to be around 40 kJ per mol H_2 in order to result in a free enthalpy of zero at ambient temperature and pressure. An overview of the hydrogen contents of the known complex metal hydrides together with the hydrogen content of the reversible ones are given in Table I. The only complex hydrides with decomposition enthalpies approaching the required value, and are therefore reversible hydrogen storage materials, are NaAlH_4 and KAlH_4 . NaAlH_4 with a ΔH for the first decomposition step of 37 kJ

TABLE I. Hydrogenation properties of complex metal hydrides

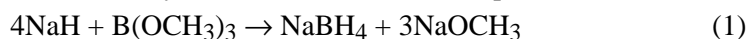
Hydride	Molecular weight g mol^{-1}	Hydrogen content wt. %	Reversibility	Reversible H_2 content, wt. %
LiBH_4	21.78	18.5	+	Unknown ⁵
NaBH_4	37.83	10.7	-	-
KBH_4	53.90	7.4	-	-
LiAlH_4	37.95	10.6	-	-
NaAlH_4	54.00	7.4	+	4.0-4.9 ⁶
KAlH_4	70.11	5.7	+	> 3.5 ⁷
$\text{Mg}(\text{AlH}_4)_2$	86.33	9.3	-	-
$\text{Ca}(\text{AlH}_4)_2$	102.01	7.8	-	-
$\text{LiMg}(\text{AlH}_4)_3$	124.28	9.7	-	-
Na_3AlH_6	102.00	5.9	+	2.1-2.3 ⁸
$\text{Na}_2\text{LiAlH}_6$	85.95	6.3	+	2.2-2.4 ⁸

mol⁻¹ is presently the most promising of the reversible complex hydrides for hydrogen storage. It has been widely studied during the last decade¹ and thus this contribution will have as its main focus recent developments concerning this material.

2. SYNTHESIS OF COMPLEX METAL HYDRIDES

The two commercially most important complex hydrides are NaBH₄ and LiAlH₄, both of which are used mainly as selective reducing agents in organic chemistry. For NaBH₄, over 100 methods of preparation have been described, but only two have reached practical significance.

In the Schlesinger process, trimethyl borate [B(OCH₃)₃] is boiled together with sodium hydride (NaH) in hydrocarbon oil at 250 °C, Eq. (1):



The addition of water hydrolyzes the NaOCH₃ to sodium hydroxide and methanol and causes the separation from the hydrocarbon oil. Methanol is recovered by distillation and recycled to form trimethyl borate. The NaBH₄ left in the sodium hydroxide solution is extracted with isopropyl amine.

The Bayer process employs the borosilicate Na₂B₄O₇·7SiO₂, which is produced by the fusion of borax and silica. The borosilicate is reacted with sodium in an atmosphere of 0.30 MPa of hydrogen at 400–500 °C. Extraction with liquid ammonia under pressure yields NaBH₄.

Sodium borohydride is the starting compound for the synthesis of all other borane-based complex hydrides. Ball-milling with lithium chloride or bromide leads to the formation of LiBH₄. The side product, *i.e.*, the corresponding sodium halide, is the thermodynamic driving force for the reaction. For the production of KBH₄, NaBH₄ is reacted with potassium hydroxide in an aqueous solution; again, the formation of side product, sodium hydroxide, is the driving force.

LiAlH₄ is industrially produced from lithium hydride (LiH) and aluminium trichloride (AlCl₃) in ether solution, Eq. (2):



Alternatively, it can be obtained metathetically from NaAlH₄ and LiCl by ball-milling. In addition, here, the formation of the side-product, sodium chloride, a thermodynamic sink, makes the procedure applicable to most of the other alanates.

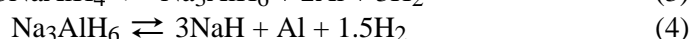
Sodium aluminohydride is usually synthesized from the elements at 100–200 °C and under 10–20 MPa of hydrogen pressure in a hydrocarbon solvent using triethyl aluminium as a catalyst.

3. COMPLEX METAL ALUMINOHYDRIDES (ALANATES)

3.1. Sodium aluminohydride

As mentioned above, sodium aluminohydride (NaAlH₄) is presently the most promising reversible complex hydride for hydrogen storage. It has a reversible

storage capacity of 5.5 wt.%, whereas its total hydrogen content amounts to 7.4 wt.%. Reversible thermal dissociation occurs in two steps *via* hexahydridoaluminate (Na_3AlH_6) as an intermediate to sodium hydride $[\text{NaH}]$ and aluminium, Eqs. (3) and (4).



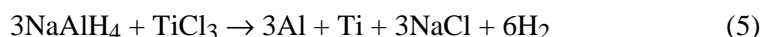
Both steps are reversible, while a third possible step, the decomposition of NaH , is possible only at much higher temperatures.

Doped sodium alanate exhibits in the first dissociation step an equilibrium pressure of 0.10 MPa at $\approx 36^\circ\text{C}$ (37 kJ/mol) and in the second at $\approx 116^\circ\text{C}$ (47 kJ/mol). Thus, NaAlH_4 is a typical low-temperature hydride, whereas Na_3AlH_6 is classified as mid-temperature hydride.^{8,9}

Although NaAlH_4 is the only known alanate with reasonable thermodynamics for use in combination with PEMFCs, it was not considered as a potential hydrogen storage material for a long time. The reported conditions for the rehydrogenation (200–400 $^\circ\text{C}$, 10–40 MPa) were simply too severe, while the kinetics were far too slow. This situation changed in 1997 with the discovery of Bogdanović and Schwickardi^{8,9} that doping NaAlH_4 with small amounts of titanium allowed rehydrogenation of the material under much milder conditions (see below). This initiated an intensive research of the material and especially the search for more efficient dopants or doping methods.

3.2. Doping agents and methods

Nowadays, titanium trichloride (TiCl_3) is generally the standard doping agent for NaAlH_4 and high-energy ball-milling, introduced in 1999, appears to be the prevalent method.¹⁰ The doping of NaAlH_4 with TiCl_3 is expressed by Eq. (5):



Titanium and aluminium are both reduced to the zero-valent state by the hydride species, which results in irreversible hydrogen evolution. For this reason, apart from the additional dead weight of the dopant, the theoretical capacity of 5.5 wt.% cannot be attained with doped samples. Therefore, the optimum doping amount is always a compromise. The more dopant that is added, the higher are the kinetic rates, but the lower is the capacity. Usually, doping levels of 2–4 mol% are considered as reasonable.

The beneficial effect of titanium on the desorption rates of alanates had been known for a long time, *i.e.*, for LiAlH_4 , but research on alternative doping materials or methods was almost non-existent. Screening of different elements as doping agents commenced only after the disclosure of the efficacy of titanium. The most investigated alternative dopants were iron and zirconium. For a long time, titanium seemed to be the most favourable doping element, as regards kine-

tics and storage capacities, so research focused mainly on different titanium precursors and doping procedures.^{11,12} In the original work, a wet chemical method was adopted and employed titanium butoxide in THF solution but today high-energy ball-milling has been demonstrated to be the more convenient preparation route and also to deliver materials with more favourable properties. For instance, the kinetic rates of NaAlH₄ doped with TiCl₃ by ball-milling are about one order of magnitude higher than those of NaAlH₄ wet chemically doped with Ti butoxide.

Therefore, apart from the doping procedure, also the nature of the titanium precursor is important for the performance of the material. Titanium halides show more favourable kinetic behaviours than those of titanium alkoxides. Titanium trifluoride shows the highest storage capacities of these halides, since the added dead weight is the lowest but, for cost reasons, titanium trichloride has emerged as the standard material. Since the use of cationic titanium sources incurs the problem that reduction to the zero valent state consumes hydrogen, which decreases the storage capacity drastically, Ti sources have been investigated. Ti₁₃ clusters, stabilized by THF, are the most prominent candidates;¹³ NaAlH₄ doped with these clusters has indeed a very high capacity and, more interestingly, extremely fast kinetics. Unfortunately, the rates decrease drastically after about five cycles and then the materials do not show any superior properties over TiCl₃-doped materials. In addition, the high costs of the clusters disqualify them for large-scale applications.

According to recent results compounds of elements other than titanium have shown good prospects as doping agents; ScCl₃ and CeCl₃ are prime examples.¹⁴ Sodium aluminohydride doped with scandium (Fig. 1) has higher kinetic rates than the titanium-doped equivalent, and also provides higher storage capacities (4.0–4.9 wt.%).

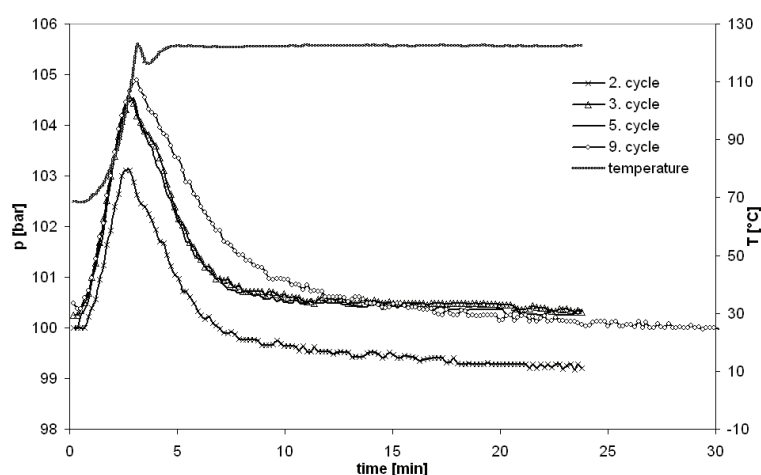


Fig. 1. Hydrogenation curves of a Sc-doped NaAlH₄ cycle test (10 MPa, 120 °C).¹⁴

With sodium aluminohydride doped with scandium (4 mol%), hydrogenations are accomplished in 4–12 min.¹⁴ The thus attained hydrogenation times approach those required for the refuelling of the future hydrogen powered fuel cell cars of 3 min. In order to check the cycle stability of the Ce-doped material, a sample (2.1 g) was tested in a 95 cycles test at 60–150 °C and 5–10 MPa (Fig. 2) and proved to be stable during this treatment. It should, however, be pointed out that removal of the hydrogenation heat by cooling in such a short time represents a tremendous technical challenge.¹⁵ In any event, both materials (Sc- and Ce-doped NaAlH₄) are extremely more expensive than titanium, hence, most probably, they will not be employed in industrial-scale applications. Accordingly, in most of the studies, TiCl₃ remains the standard doping agent.

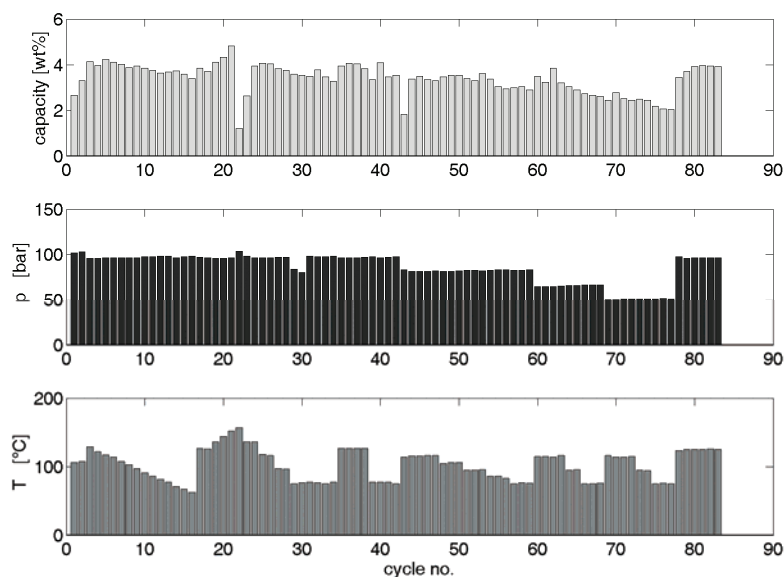


Fig. 2. Course of a 83-cycle test of Ce-doped NaAlH₄.¹⁴

3.2.1. State of titanium in doped NaAlH₄

The exact nature of titanium and its catalytic properties in the Ti–NaAlH₄ system are still not fully understood. It is even unclear whether Ti acts as a true catalyst. Nevertheless, many facts have been clarified that help to compose a clear picture of the system.

Measurements of the hydrogen evolved during ball-milling of several dopants with sodium alanate show clearly that the dopants are reduced to the zero-valent state, as formulated in Eq. (5). This finding is supported by several XRD and XAS studies. Similar studies with stoichiometric mixtures of LiAlH₄ with TiCl₃ and TiCl₄ demonstrated the formation of Ti–Al alloys. Although these alloys could not be clearly identified for NaAlH₄ reacted with TiCl₃ in sub-stoi-

chiometric amounts, some supporting evidence exists. The aluminium reflection in XRD patterns of dehydrogenated Ti-doped NaAlH_4 samples show a slight shoulder, which suggests the existence of an Al_3Ti alloy. In addition, if the remaining NaAlH_4 is leached out after ball-milling with THF and the remaining solid is treated at elevated temperatures, Al_3Ti can be detected by XRD analysis. This result corresponds to the findings from XAS experiments. Analysis of the XANES and EXAFS region of the spectra suggests an Al_3Ti -like local environment of titanium in freshly ball-milled, dehydrogenated and hydrogenated samples.^{16–18} Thus, even if an Al–Ti alloy is not formed during the doping process, probably on account of too low a temperature, there is substantial information to indicate that the titanium is reduced and dispersed into the aluminium phase and does not affect the alanate lattice. Such behaviour is also supported by XRD measurements, the NaAlH_4 lattice parameters remain exactly the same for doped and undoped materials. Additionally, TEM–EDX measurements confirm that titanium is only associated with the aluminium phase in the dehydrogenated material – hydrogenated materials would be decomposed by the electron beam and therefore cannot be evaluated by TEM. In summary, it can be concluded that titanium is reduced to the zero-valent state during doping and is dispersed in the aluminium phase. This ‘solid solution’ is a separate phase from the NaAlH_4 lattice, which is thereby unaffected by the presence of titanium.

3.2.2. Mechanistic aspects of titanium doping

Although the location of the titanium and its oxidation state in the system has been investigated very thoroughly, the mechanism of the facilitated hydrogen uptake and release has yet to be fully elucidated. The first problem in understanding the processes occurring is the spatial distance between the active species, the Ti–Al solid solution and the hydrogen-storage material (NaAlH_4). Transmission electron micrographs (TEM) of dehydrogenated samples show micrometer-sized aluminium particles decorated with NaH crystallites (Fig. 3). Since a

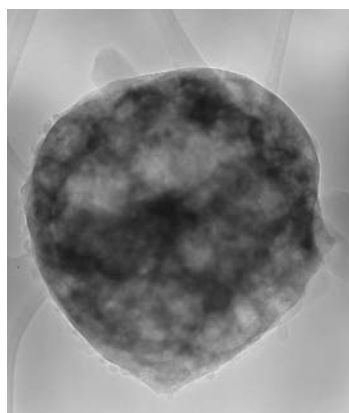


Fig. 3. TEM Microphotograph of decomposed titanium-doped sodium alanate.

complete hydrogenation of the sample takes about 5 min in optimized samples, mass transfer of sodium and/or aluminium must occur over micrometer distances during the same period of time.

Transportation *via* mobile AlH_3 was proposed as another possible explanation for the enhanced transfer rates. Indeed, inelastic neutron scattering spectroscopy experiments have shown that a volatile molecular aluminium hydride is formed during the early stage of hydrogen uptake by dehydrogenated titanium-doped NaAlH_4 .¹⁹

3.3. Other alanates

3.3.1. Lithium aluminohydride

Lithium aluminohydride (LiAlH_4), which has been studied extensively as a selective hydriding agent in organic chemistry, is an irreversible hydrogen storage material. This, together with the high cost of lithium, disqualifies the material for large-scale storage applications despite the fact that its theoretical capacity of 7.9 wt.% over the first two decomposition steps is extraordinarily high.

The alanate is thermodynamically unstable and decomposes below room temperature. The decomposition of LiAlH_4 is kinetically hindered, however, so that it is metastable at room temperature, even when ball-milled.²⁰ Interestingly, ball-milling with titanium compounds leads to a partial release of hydrogen during the doping procedure itself. This implies that the catalytic effect of titanium on the decomposition of alanates is restricted not only to NaAlH_4 but seems to be a more general phenomenon. It is deduced, therefore, that titanium acts predominantly on the $(\text{AlH}_4)^-$ or $(\text{AlH}_6)^{3-}$ species.

3.3.2. Potassium aluminohydride

Like NaAlH_4 , potassium aluminohydride (KAlH_4) is a reversible hydrogen-storage material.⁷ It even takes up and releases hydrogen without any aid of an external catalyst. This is significantly different from the reaction mechanism of NaAlH_4 or LiAlH_4 . Nevertheless, the decomposition proceeds *via* the same pathway. The hexahydride (K_3AlH_6) is formed in the first decomposition step, which further decomposes to KH and finally to potassium metal. As with the NaAlH_4 system, the last step is not reversible. The theoretical storage capacity over the first two decomposition steps of KAlH_4 amounts to 4.3 wt.%, which is only 77 % of the value for NaAlH_4 .

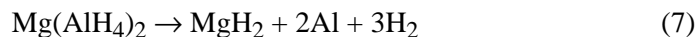
The conditions for the dehydrogenation and rehydrogenation reactions also differ significantly from NaAlH_4 . The hydrogen pressures for both steps are lower than 1 MPa, which makes the system easier to handle, but the required temperatures are in the range of 300–350 °C. A possible lowering of these temperatures by the addition of catalysts has not been reported.

3.3.3. Magnesium aluminohydride

Magnesium alanate can be easily prepared by a metathesis reaction starting from MgCl_2 and two moles of NaAlH_4 :²¹



The reaction can be performed in the solid state through ball-milling or in ether solution as a wet chemical reaction. In the latter case, etherates are the final products, which decompose at elevated temperatures under vacuum to the complex hydride. Magnesium alanate is a complex metal hydride with a high hydrogen content (7.0 wt.%) for the decomposition reaction expressed by Eq. (7):

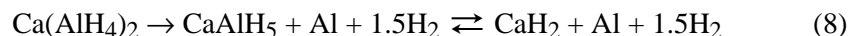


At temperatures around 130 °C, three moles of hydrogen are released in a one-step mechanism.

Compared with the alkaline alanates LiAlH_4 , NaAlH_4 and KAlH_4 , no hexahydride intermediate can be observed. The final products of the thermal decomposition are MgH_2 and aluminium metal. The decomposition enthalpy of $\text{Mg}(\text{AlH}_4)_2$ is around 0 kJ mol⁻¹, which means that the equilibrium pressure of $\text{Mg}(\text{AlH}_4)_2$ is extremely high (calculated from the Van't Hoff equation). This alanate is therefore too unstable for reversible de- and re-hydrogenation reactions and cannot be used under technical conditions in combination with a PEMFC.

3.3.4. Calcium aluminohydride

The metathesis reaction between CaCl_2 and two moles of NaAlH_4 can be employed for the preparation of calcium alanate, $\text{Ca}(\text{AlH}_4)_2$. Ball-milling produces the alanate in combination with NaCl as a by-product. Wet-chemical preparation in ether solution produces the etherate product, which decomposes at elevated temperatures under vacuum to the pure alanate.²² Three moles of hydrogen are released during the first two decomposition steps according to Eq. (8):



During both decomposition steps, 1.5 moles of hydrogen are released. The intermediate product CaAlH_5 has an octahedral structure, which is interconnected over two corners producing long chains (see Fig. 4).²³ From thermodynamic measurements, it has been shown that the first decomposition step of $\text{Ca}(\text{AlH}_4)_2$ is exothermic and cannot be used in reversible re- and de-hydrogenation reactions. The second step is endothermic and, in principle, is reversible under acceptable technical conditions.

4. COMPLEX METAL BOROHYDRIDES

Complex metal borohydrides,²⁴ of which the most commonly used is NaBH_4 , are materials with a high hydrogen content (10.8 wt.% for NaBH_4 , see Table 1),

but they mainly show unfavourable thermodynamics and can, therefore, not be used as reversible hydrogen-storage materials. The thermal decomposition reaction is different compared to the complex metal aluminohydrides and no hexahydride intermediate product has been observed. The final products of the decomposition are a binary metal hydride and elemental boron metal, Eq. (9):

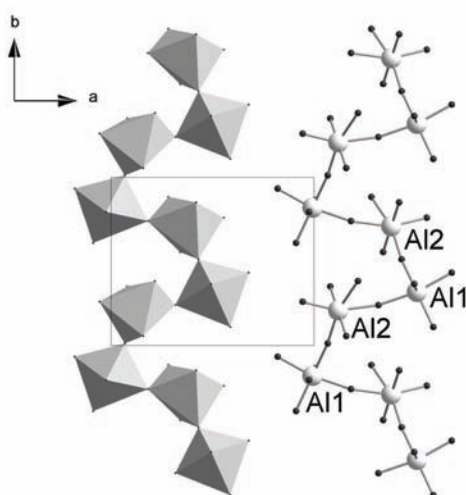
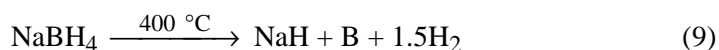


Fig. 4. Crystal structure of interconnected octahedral AlH_6 units in CaAlH_5 .

The thermal decomposition temperature of NaBH_4 is around $400\text{ }^\circ\text{C}$, *i.e.*, much too high for PEMFC applications. Traces of boron hydrogen compounds (B_xH_y) produced during the thermal decomposition are problematic because they can poison the fuel cell catalyst and also damage the membrane. Therefore, complex borohydrides are used for the production of hydrogen *via* a hydrolysis reaction with water.²⁵ In the presence of a ruthenium catalyst, dissolved NaBH_4 decomposes into hydrogen with the production of sodium metaborate, NaBO_2 , as the final product. Half of the evolved hydrogen comes from the water and thus increases the storage capacity of the system (Eq. (10)). In principle, only two moles of water are required for a complete decomposition of NaBH_4 but, in practice, the solubilities of NaBH_4 and, more importantly, of NaBO_2 are the limiting factors of the storage capacity. Sodium metaborate has a solubility of only 26 g per 100 ml in water at $20\text{ }^\circ\text{C}$. To prevent precipitation from the solution and the blocking of the active sites of the catalyst, the NaBH_4 concentration must be lower than the maximum solubility of the metaborate. A typical composition of a commercial NaBH_4 aqueous solution is 20 wt.% NaBH_4 and 1 wt.% NaOH for stabilization of the solution. This reduces the storage capacity to 4 wt.% for the whole hydride system.



The operation of a commercial NaBH₄ solution and PEMFC system is shown schematically in Fig. 5. The NaBH₄ solution is stored in a tank and converted into hydrogen when required in the catalyst chamber. The amount of hydrogen produced can be controlled by the flow of the fuel solution into the catalyst chamber. The hydrogen gas and the decomposition product (NaBO₂) are separated in the gas–liquid separator. After separation from the sodium metaborate by-product, which is stored in a second fuel tank, the hydrogen is fully humidified and can be used for the production of energy in the fuel cell. The amount of hydrogen depends on the quantity of NaBH₄ solution that is pumped into the catalyst chamber and on the electric power demanded from the fuel cell.

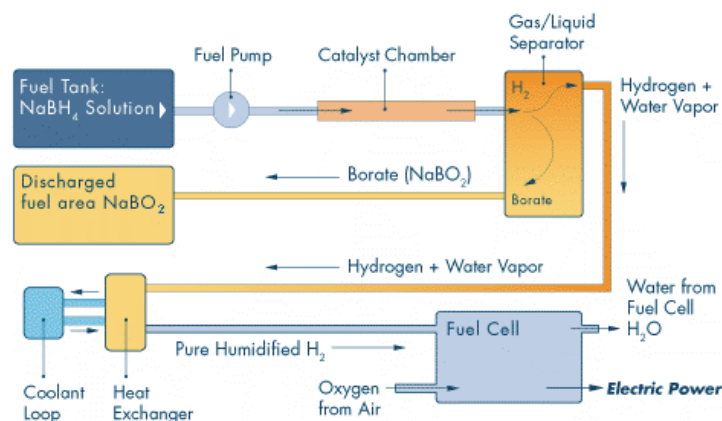


Fig. 5. Operating scheme of a commercial NaBH₄–PEMFC system (Millennium-Cell).

Significant barriers for a broad introduction of NaBH₄ as a hydrogen-releasing material are the high price for the desorbed hydrogen and the regeneration of the hydride from the metaborate solution outside the fuel cell system. Different methods have been described in the literature but several technical points have still to be resolved. Nevertheless, the storage in, and release of hydrogen from, NaBH₄ solutions is interesting for a wide range of applications.

One other borohydride with a high hydrogen content is LiBH₄, which has a capacity of more than 18 wt.% H₂.²⁶ Again, the decomposition temperature (≈ 380 °C) is too high for usage with a PEMFC and the material is not reversible under acceptable practical conditions. With the addition of a second material to the lithium borohydride, the decomposition pathway may be changed together with the thermodynamics of the system (thermodynamic tailoring).



A reaction mixture of two moles LiBH₄ and one mole MgH₂, Eq. (11), has a theoretical hydrogen storage capacity of 11.4 wt.%. This is lower than that for

pure LiBH_4 but the decomposed mixture can be re-hydrogenated at temperatures of 230–250 °C under a hydrogen pressure of 10 MPa. Unlike LiBH_4 , where elementary boron is the final product of the decomposition, the final product of the LiBH_4 – MgH_2 mixture is magnesium boride MgB_2 . This different reaction pathway stabilizes the right side of the reaction, which means that the left side is destabilized and the reaction becomes reversible. It has been shown that such a mixture could reversibly store up to 8 wt.% of hydrogen.²⁷ The hydrogenation conditions are far removed from technical requirements, but these experiments show that thermodynamic properties can be changed by the addition of a second component to the complex metal hydride.

5. CONCLUDING REMARKS

The advances in the research on complex metal hydrides for hydrogen storage over the last couple of years are remarkable. The properties of some systems are approaching the requirements for large-scale applications, set as targets by the DOE (Department of Energy).

Today, doped NaAlH_4 is still the most promising material to meet most of these targets. It decomposes sufficiently quickly to provide adequate hydrogen during all operation states of the fuel cell, which include peak power demand. The temperature required for the decomposition rates is low enough to be provided for by the waste heat of the fuel cell. In addition, the kinetics for the refueling meets the DOE-targets; re-hydrogenation times of less than five minutes have been measured for optimized systems. Additionally, the cycle stability of doped NaAlH_4 is high – no changes in performance and capacity could be observed in over 100 measured cycles.

Considering the rate of progress over recent years, a further increase of the limits is to be expected. It must be recognized, however, that the theoretical limits cannot be shifted. The theoretical hydrogen storage capacity of 5.5 wt.% is definitely considered by various organizations and industrial companies to be too low for large-scale applications. In addition, the requirements for cooling during refuelling due to the thermodynamics of the re-hydrogenation are too severe. Therefore, realistically, even NaAlH_4 , which is presently the most promising candidate material, will not meet all the criteria necessary to provide a practical means of hydrogen storage. For reversible storage capacities over 5 wt. %, other options will have to be explored.

ИЗВОД

СКЛАДИШТЕЊЕ ВОДОНИКА У КОМПЛЕКСНИМ МЕТАЛНИМ ХИДРИДИМА

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Комплексни метални хидриди, као што су натријум-алуминијум-хидрид (NaAlH_4) и натријум-бор-хидрид (NaBH_4), су чврсти материјали за складиштење водоника са високим капацитетом. Они се могу користити у комбинацији са горивим спрегивима као извор водоника, чиме се обезбеђује дужи рад него са класичним металним хидридима. За широку примену ових материјала најважнија је реверзибилност у умереним условима коришћења. За сада једино NaAlH_4 има задовољавајуће термодинамичке особине и може се применити као термодинамички реверзибилан вид складиштења водоника. Насупрот њему, NaBH_4 је типичан иреверзибилни комплексни метални хидрид; он реагује са водом и производи водоник.

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REFERENCES

1. F. Schüth, B. Bogdanović, M. Felderhoff, *Chem. Commun.* (2004) 2249
2. M. Fichtner, *Ann. Chim.* **30** (2005) 483
3. B. Bogdanović, G. Sandrock, *MRS Bulletin* (2002) 712
4. W. Grochala, P. P. Edwards, *Chem. Rev.* **104** (2004) 1283
5. Y. Nakamori, G. Kitahara, G. Miwa, N. Ohba, S. Towata, A. Züttel, S. Orimo, *J. Alloys Compd.* **404–406** (2005) 396
6. B. Bogdanović, M. Felderhoff, A. Pommerin, F. Schüth, N. Spielkamp, *Adv. Mater.* **18** (2006) 1198
7. H. Morioka, K. Kakizaki, S. Ch. Chung, A. Yamada, *J. Alloys Compd.* **353** (2003) 310
8. B. Bogdanović, M. Schwickardi, *J. Alloys Compd.* **253–254** (1997) 1
9. B. Bogdanović, R. A. Brand, A. Marjanović, M. Schwickardi, J. Tölle, *J. Alloys Compd.* **302** (2000) 36
10. A. Zaluska, I. Zaluski, J. O. Ström-Olsen, *J. Alloys Compd.* **298** (2000) 125
11. R. A. Zidan, S. Takara, A. G. Hee, G. M. Jensen, *J. Alloys Compd.* **285** (1999) 119
12. C. M. Jensen, K. J. Gross, *Appl. Phys. A* **72** (2001) 213
13. R. Franke, J. Rothe, J. Pollmann, J. Hormes, H. Boennemann, W. Brijoux, Th. Hindenburg, *J. Am. Chem. Soc.* **118** (1996) 12090
14. B. Bogdanović, M. Felderhoff, A. Pommerin, F. Schüth, N. Spielkamp, A. Stark, *J. Alloys Compd.* (2008), doi:10.1016/j.jallcom.2008.03.106
15. M. Felderhoff, C. Weidenthaler, R. von Helmholt, U. Eberle, *Phys. Chem. Chem. Phys.* **9** (2007) 2643
16. M. Felderhoff, K. Klementiev, W. Grünert, B. Spliethoff, B. Tesche, J. M. Bellosta von Colbe, B. Bogdanović, M. Härtel, A. Pommerin, F. Schüth, C. Weidenthaler, *Phys. Chem. Chem. Phys.* **6** (2004) 4369
17. J. Graetz, J. J. Reilly, J. Johnson, A. Yu Ignatov, T. A. Tyson, *Appl. Phys. Lett.* **85** (2004) 500
18. A. Léon, O. Kircher, J. Rothe, M. Fichtner, *J. Phys. Chem. B* **108** (2004) 16372
19. Q. J. Fu, A. J. Ramirez-Cuesta, S. C. Tsang, *J. Phys. Chem. B* **110** (2006) 711
20. H. W. Brinks, B. C. Hauback, P. Norby, H. Fjellvåg, *J. Alloys Compd.* **351** (2003) 222
21. M. Mamatha, B. Bogdanović, M. Felderhoff, A. Pommerin, W. Schmidt, F. Schüth, C. Weidenthaler, *J. Alloys Compd.* **407** (2006) 76

22. M. Fichtner, C. Frommen, O. Fuhr, *Inorg. Chem.* **44** (2005) 3479
23. C. Weidenthaler, T. J. Frankcombe, M. Felderhoff, *Inorg. Chem.* **45** (2006) 3849
24. L. Laversenne, B. Bonnetot, *Ann. Chim.* **30** (2005) 495
25. S. C. Amendola, S. L. Sharp-Goldmann, M. S. Janjua, N. C. Spencer, M. T. Kelly, P. J. Petillo, M. Binder, *Int. J. Hydrogen Energy* **25** (2000) 969
26. A. Züttel, P. Wenger, S. Rentsch, P. Sudan, P. Mauron, C. Emmenegger, *J. Power Sources* **118** (2003) 1
27. J. J. Vajo, S. L. Skeith, F. Mertens, *J. Phys. Chem. B* **109** (2005) 3719.