Polish J. Chem., **79**, 1087–1092 (2005) **COMMUNICATION**

Thermal Decomposition of Chemical Hydrides[*]

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(Received October 29th, 2004)

The temperature, T_{dec}, at which a binary chemical hydride decomposes to its constituent metallic or nonmetallic element and molecular hydrogen represents one important indicator for its potential use as a hydrogen-storage material for mobile and stationary applications [2]. Ideally, T_{dec} for a hydride should be within the range 60–100°C for use with a polymer electrolyte (proton exchange) membrane fuel cell [3]. So far there were no simple guidelines to rationalise the wide variation in T_{dec} amongst the binary hydrides of the chemical elements. Recently, Grochala and Edwards have found a surprisingly simple correlation between T_{dec} and a widely-recognised and a characteristic property of the metal or nonmetal center bound to the hydride ion in MH_n species, *viz*. the value of the standard redox potential, E^0, for the M^{n+}/M^0 redox pair in acidic aqueous solutions [4].

In Figure 1 is shown the dependence of T_{dec} with E^0 assembled for a wide range and variety of binary hydrides of metallic and nonmetallic elements notably: Li, Na (monohydrides), Be, Mg, Ca, Sr, Ba, V, Zn, Cd, Hg (dihydrides), B, Al, Ga, Y, Er, U, Pu, P, Sb (trihydrides), and Sn (tetrahydride). The thermal decomposition of a binary hydride, described by the general equation: $M^{n+}(H^{-1})_n \rightarrow M^0 + n/2\ H_2$, is facile (thermodynamically and kinetically) for chemical hydrides containing electronegative metal cations such as Hg^{2+}, Sb^{3+} *etc.*, which facilitate the oxidation of hydride anions, but inhibited for hydrides containing electropositive cations which are difficult to reduce (such as Li^+, or Ba^{2+}).

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[*] This paper is dedicated to memory of Professor Piotr K. Wrona, eminent Polish inorganic electrochemist [1].

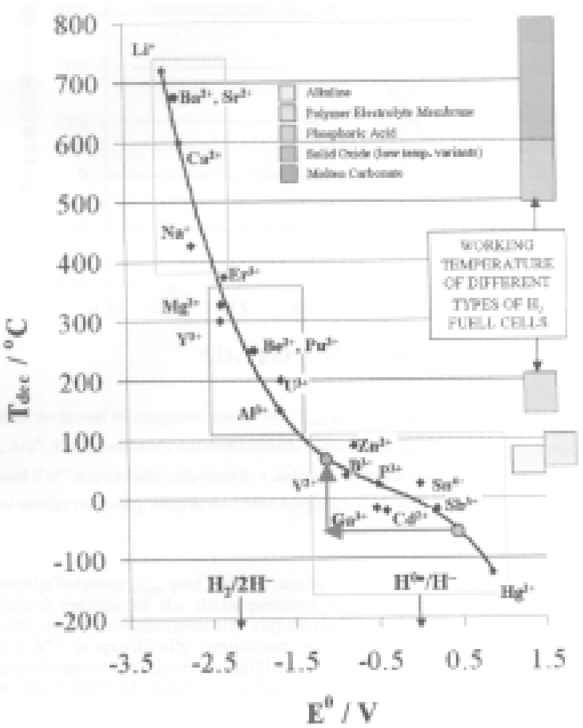

Figure 1. Correlation between the temperature, T_{dec}, at which thermal decomposition of binary hydrides MH_n to the constituent elements proceeds, and the corresponding standard redox potential of the M^{n+}/M^0 redox pair in the acidic aqueous solution, E^0, *vs.* NHE. Hydrides which store hydrogen reversibly are those in the top box. Hydrides reversible only under large or extreme pressures are shown in the middle box. Hydrides storing hydrogen irreversibly are those in the bottom box. Symbols of chemical elements together with their formal valence are shown for chosen hydrides. The ranges of the working temperatures for prototypical of fuel cells are also shown. The E^0 values for $H_2/2H^-$ and $H^{0\bullet}/H^-$ redox pairs are indicated. Thermal stability of a binary hydride (point between Sb^{3+} and Hg^{2+}) may be increased by complexing of the M^{n+} cation with chelate ligands (point between B^{3+} and Al^{3+}); this results in a decrease of the E^0 value (as shown by arrows).

The relationship between T_{dec} and E^0 holds over a range of some 850 K in T_{dec}, and over 4 V in E^0; it may be rationalized in terms of the red-ox (electron transfer or reductive H_2 addition) reaction, by a model of avoided-crossing between electronic states of the central metal or nonmetal and hydrogen [5]. The detailed analysis of the relationship between T_{dec} and E^0, possible exceptions from this behaviour for binary hydrides, and extension of the presented relationship to ternary and complex hydrides, have been discussed in detail elsewhere [4].

Another correlation of the utmost importance for control of the T_{dec} value – obviously interrelated with the one from Figure 1 – is that between T_{dec} and ΔH_f^0 (standard enthalpy of a hydride formation *per one mole* of H) [4]. It is shown in Figure 2.

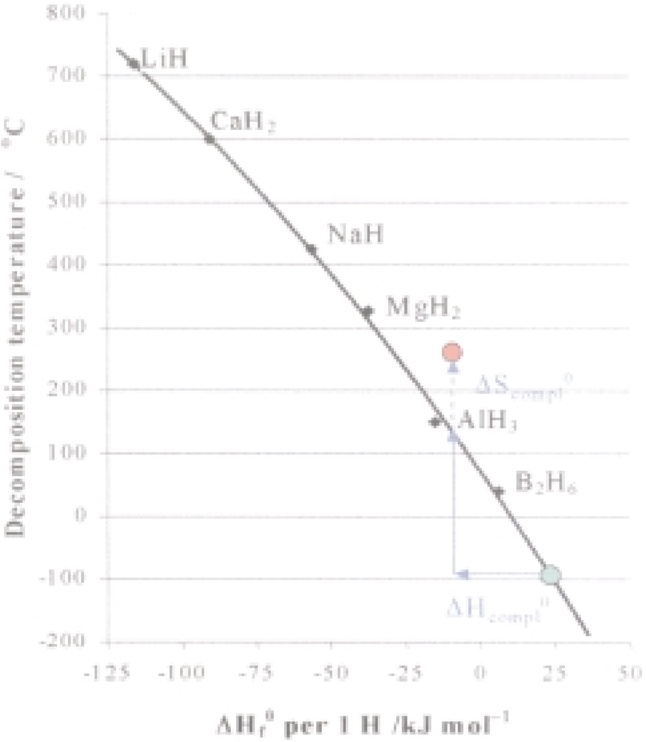

Figure 2. Correlation between the thermal decomposition temperature, T_{dec}, and the corresponding standard enthalpy of a hydride formation per one mole of hydrogen, ΔH_f^0. The T_{dec} value of a thermodynamically and thermally unstable hydride of a metal cation M^{n+} (lower circle) can be *substantially* increased if M^{n+} is specifically complexed by a chelate ligand (upper circle). Novel hydride results of increased thermodynamic and thermal stability (red point), while its free Gibbs energy benefits from both the enthalpy and entropy of complexation (as indicated by arrows).

Note that the relationship between T_{dec} and ΔH_f^0 is nearly linear, due to predominant contribution of the entropy of gaseous H_2 to the standard entropy of the decomposition reaction (most of important hydrogen stores are solids). Importantly, the T_{dec} value of a thermodynamically and thermally rather unstable hydride of a metal cation M^{n+} can be *substantially* increased if M^{n+} is specifically complexed, particularly by a chelate ligand, L. Novel hydride, $\{ML\}H_n$, results of increased thermodynamic and thermal stability, while its free Gibbs energy benefits from both the enthalpy and entropy of complexation (see Figure 2). Analogous effect in terms of the decrease of the E^0 value is shown in Figure 1.

It seems at the first sight that several binary and ternary hydrides have attractive values of T_{dec} for their potential incorporation into low-temperature fuel cells. Thus, one identifies ZnH_2 (T_{dec} = 90°C, 3.0 weight % hydrogen), the borohydride $Zn(BH_4)_2$ (T_{dec} = 85°C, 8.4 wt %), the potassium-silicon(II) hydride $KSiH_3$ (T_{dec} = 70°C, 4.3 wt %), CuH (T_{dec} = 60°C, 1.5 wt %), or the lithium gallium(III) hydride $LiGaH_4$ (T_{dec} = 50°C, 3.7 wt %). Unfortunately, these compounds, with the possible exception of zinc borohydride [6], cannot store a sufficiently high weight % of hydrogen (for example, to come close to the U.S. DOE target value of 6.5 wt%), their decomposition is kinetically irreversible, and their production is expensive. Thus, necessity appears of applying *catalysts* of H_2 evolution and reabsorption in combination with the highly efficient hydrogen stores.

Classical hydrogen stores, which constitute natural environment in which prospective catalysts of the H_2 evolution and reabsorption are finely dispersed, are the powerfully reducing chemical species (typically $M(H)_n$, $M(AlH_4)_n$, or $M(BH_4)_n$, where M = Li, Na, Mg, Al *etc*.). Remarkably, the E^0 values of hydrogen stores are typically lower than –1.5 V and can exceed –2.5 V in some cases. The list of chemical species which could withstand such ruthless conditions is, of course, enormously limited. Idea arises to use systems allowing for a *reversible* $2e^-$ redox reaction while shifting the whole process into the region of strongly negative E^0 values (by chelating of the metal cations involved in catalytic process [7]). Strength of the complexation of a metal cation involved in catalytic process should be adjusted very precisely (so that catalytic activity is not lost), and should be different for each cooperating hydrogen store. Indeed, the thermodynamic stability of an oxidized form of a catalyst should be similar (and only slightly smaller) than that of a hydrogen store itself, thus allowing for the efficient and low-barrier transfer of H_2 between hydrogen store and the gas phase (Figure 3). The hydrogen store itself should not be thermodynamically very stable, to avoid costful enthalpic effects while decharing the reservoir, and thermal overrun while charging it [8]. The reduced form of a catalyst should coexist with an empty hydrogen store, while thermal H_2 desorption should take place through the oxidized form of the catalyst (the latter should coexist with a charged hydrogen store). Importantly, even the reduced form of a catalyst – if it still contains metal species in a positive oxidation state – should not be further irreversibly reduced by – once decomposed – hydrogen store, a task which is not easy to meet (typically a reactive and very electropositive metal, such as Li, Mg, Al, or their mixture, and sometimes a secondary very stable hydride, such as LiH [9] or NaH, result from the decomposition of hydrogen stores).

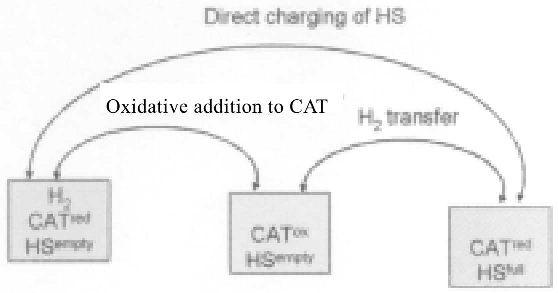

Figure 3. Scheme of the catalytic action in the process of H_2 reabsorption and evolution from the hydrogen store (HS), facilitated by a catalyst (CAT). "red" stands for the reduced, and "ox" for the oxidized form of the catalyst. Note that both processes involved in the catalytic pathway of the reaction should be not far from the thermodynamic equilibrium at ambient conditions (p = 1 atm, T = 25°C), so that the reabsorption of H_2 can occur under small H_2 overpressure (several bar), while H_2 evolution can take place at relatively low temperature (60–90°C).

The present correlations (Figures 1 and 2) suggest that use of compounds of Ga^{3+} [10], V^{3+}, Cr^{3+}, V^{2+}, Cr^{2+}, and particularly those of cheap and readily-available metals or semimetals, Ti^{4+} [11], Ti^{2+}, Fe^{2+}, Ni^{2+}, Si^{4+} [12], Si^{2+}, and Ge^{2+}, as catalysts for hydrogen evolution from the cheapest hydrogen stores, such as $NaBH_4$ (< \$100 per 1 kg of stored hydrogen), NaH, $LiAlH_4$ or MgH_2, may be a highly effective route toward these targets.

Thus, high storage capacity and moderate kinetic reversibility of hydrides of light, highly-electropositive metals (*e.g.* MgH_2) might ultimately be married with the low decomposition temperature of hydrides of the more electronegative chemical elements of the Periodic Table. This will allow to deliberately tune up the value of T_{dec} [13] toward the desired temperature region of 60–100°C, and provide the dream hydrogen store for the transportation of the future [14].

Acknowledgments

I gratefully acknowledge the Polish State Committee for Scientific Research, (KBN Grant 4 T09A 017 23) for the financial support, and NATO Science for Peace Program for awarding the us the planning grant for the Highly Efficient and Terrorist-proof Hydrogen Energy Reservoir (HEATHER, SfP 980845) project; this allowed for crystallization of major ideas in design of novel catalyst, in cooperation with several teams worldwide. W.G. now holds the Fellowship of The Foundation for Polish Science.

NOTES AND REFERENCES

1. Prof. Wrona wrote in his letter to me (dated 3 Jul 2003): "Problem of the thermal decomposition temperature is interesting, and perhaps it (T_{dec}) could be formalized one day, similarly to the melting or boiling temperature". Author is now happy that the first small step was done towards achieving this goal.
2. Schlapbach L. and Züttel A., *Nature*, **414**, 353 (2001).
3. Carrette L., Friedrich K.A. and Stimming U., *Fuel Cells*, **1**, 5 (2001).
4. Grochala W. and Edwards P.P., *Chem. Rev.*, **104**, 1283 (2004).
5. Importantly, the validity of the presented relationship is additionally supported by the failure to experimentally generate the stoichiometric trihydrides of In, Tl, Bi, Sc, Ti, V, Yb and Eu, the tetrahydrides of Pb, Ti, Zr, Hf, Ce, Th, and U, and the pentahydrides of P, As, Sb and Bi. In all cases the corresponding metal cations are highly oxidizing towards H^{-1}.
6. $Zn(BH_4)_2$ is an efficient but irreversible hydrogen store (Grochala W., Edwards P.P., Harris R., Chang I.T.H., British Patent Application).
7. Ligands should not contain unsaturated bonds, as they are meant to be embedded in the strongly reducing hydrogen store. They should also be built of as light elements as possible, so that not to decrease the effective hydrogen storage capacity of the reservoir.
8. Unfortunately, due to large entropy effects connected with H_2 evolution, relatively large negative enthalpy of hydride formation is requested so that the store is thermodynamically stable.
9. The most thermally stable among the binary hydrides; it starts decomposing at 720°C, above its melting temperature, T_{melt} = 680°C (Ref. 9). Some data indicate even T_{dec} as high as 950°C.
10. The interesting Ga^{3+}/Ga^{1+} redox pair appears in electrochemistry for some compounds of Ga. For other species, this is mainly the M^{2+}/M^0 pair, which is thought to be involved in catalytic process. In principle, two concerted $1e^-$ processes (*e.g.* Ni^{2+}/Ni^{1+}, Cr^{3+}/Cr^{2+} *etc.*) can also be used for H_2 activation.
11. Indeed, indications of enhanced reversibility and lowering of the T_{dec} have been obtained by doping $NaAlH_4$ with Ti^{4+} salts: (a) Bogdanovic B. and Schwickardi M., *J. Alloys Comp.*, **253**, 1 (1997). It has been postulated that Ti nanoparticles play the role of catalyst of H_2 absorption and desorption. Similar effect has been seen for other Ti-containing systems such as TiN: (b) Bogdanovic B., Felderhoff M., Kaskel S., Pommerin A., Schlichte K. and Schüth F., *Adv. Mat.*, **15**, 1012 (2003), and recently postulated

for novel TiC nanostructures and for TiO and TiH_2: (c) Grochala W., *Chem. Comm.* (in press); (d) Feng J., Grochala W. and Hoffmann R., unpublished data.

12. SiO_2 turns out to catalyze H_2 evolution from $LiBH_4$: Züttel A., Wenger P., Rentsch S., Sudan P., Mauron P. and Emmenegger C.,*J. Power Sources*, **118**, 1 (2003). Chemical identity of a catalyst is as yet uknown.
13. T_{dec} is formally defined as the temperature at which H_2 pressure above the solid hydride equals to 1 atm. Here we show the "practical" values of T_{dec}, obtained from thermogravimetric analysis, and not from the H_2 pressure-composition isotherms.
14. The computational aspects of the chemical tuning of the thermal decomposition temperature of inorganic hydrides will be discussed elsewhere: Grochala W. and Edwards P.P.,*J. Alloys Comp*., (in press).