Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 28 (2008) 1467–1473
www.elsevier.com/locate/jeurceramsoc

Materials challenges for hydrogen storage

Z.X. Guo[a,*], C. Shang[b], K.F. Aguey-Zinsou[a]

[a] *Department of Chemistry, University College London, London WC1E 6BT, UK*
[b] *School of Environmental Sciences, University of East Anglia,*
Norwich NR4 7TJ, UK

Abstract

Undesirable climate changes due to excessive anthropogenic CO_2 emissions are of critical concern. Hydrogen as a clean energy carrier holds great promise in mitigating the problems. However, storing sufficient amount of hydrogen safely and practically poses large technical challenges, associated with materials properties that depend strongly on structure, chemistry and reaction path. Mechanical milling and chemical additions are effective in modifying various hydride systems. Considerable progresses have been achieved in improving thermodynamic and kinetic properties for hydrogen sorption. A final step to meet the technical challenges may rest with hybrid systems that can make use of modified physi- and chemi-sorptions, guided by computational simulations.

Keywords: Milling; Grain size; Chemical properties; Fuel cells; Hydrogen storage

1. Introduction

Undesirable climate change is the toughest challenge facing the human race. CO_2 emission from burning fossil fuels has been clearly identified as the main culprit for global warming. Global CO_2 emission from fossil fuel combustion increases from 20.7 billion tonnes (Gt) in 1990 to 32.5 Gt in 2006 (9.9 Gt of carbon equivalent),[1] currently growing 35% faster than expected because of inefficiency in fossil fuel use and the weakening of natural carbon sinks.[2] This has resulted in a sharp rise of atmospheric CO_2 from around 180–280 ppm in the last 400,000 years to >400 ppm in recent years (a quarter of the level that was once believed to cause extinction of all living species on land in the Triassic–Jurassic boundary, and it only takes less than 100 years to reach that level if no effective action is taken). Moreover, projected world energy demand will double by 2050, whereas available fossil fuels are likely to decline steeply after 20–30 years.[3] We are facing great challenges in sustaining increased energy demand, while improving our quality of life and protecting the environment.

Hydrogen is a clean and renewable energy carrier, ideal as a cold combustion fuel to produce electrical energy, e.g. in a fuel cell, with a high efficiency not limited by the Carnot cycle. Increasing applications of hydrogen energy is an effective way forward to mitigate climate change. Effective clean (renewable) hydrogen generation and storage are widely recognised as the two main technical issues in expanding hydrogen application. Current renewable generation technologies, such as wind, solar, biomass, tidal/wave, only provide a few % of the total energy consumption. Much R&D efforts are required to increase the efficiency and reduce the costs of the technologies.

Hydrogen as an energy carrier needs to be stored effectively and safely, particularly for vehicular applications. It may be stored as a gas, a liquid, or an atomic "solid", e.g. in a hydride. The latter represents the safest method with a relatively large H-storage capacity per unit volume, compared with all other forms of H_2. For optimum H-storage, an ideal storage system should possess: a high H-storage capacity (>6 or 9 mass% hydrogen, or 5.5 kg H_2 in a tank that can be fitted under the car seat), a low thermodynamic stability (leading to a low desorption temperature <150 °C, under a moderate pressure), high kinetics for hydrogen absorption/desorption (<1–2 mass%/min, e.g. 5 min re-filling time), high stability against O_2 and moisture (hence a long cycle life >500 cycles), good thermal conductivity (for rapid conduction of sorption heat), and low cost <£ 2.5/kWh (Fig. 1).

Various material systems have been considered to store hydrogen,[4] including $LaNi_5$,[5,6] TiFe compounds,[7,8] Mg-based

---

[*] Corresponding author. Tel.: +44 20 76797527; fax: +44 20 76797463.
E-mail address: z.x.guo@ucl.ac.uk (Z.X. Guo).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.12.019

materials,[4,9,10] and alanates,[11,12] but none meets all the above targets. Recently, several new candidates have been considered for such purposes, such as systems with a fullerene structural motif, including carbon, boron nitride, BC_3, BC_2N or composite $B_xC_yN_z$ nanotubes, or with a complex structure and reaction path, such as M–N–H (M = Li, Mg, B, etc.) and M–Al–H (M = Na, B, Li, Mg, etc) systems. These systems can have relatively large hydrogen capacities (e.g. 4.2 mass% for boron nitride nanotubes,[13] up to 10 mass% for carbon nanotubes,[14] and >10 mass% for some M–N–H[15]). The fullerene compounds possess good reversibility at relatively low temperatures but high pressures. Additionally the kinetics of charging and discharging are not particularly fast, thus limiting their practical applications. The complex/multi-component hydrides usually suffer from poor reversibility and/or complex reaction paths. The fundamental mechanisms of hydrogen binding in these systems need to be well understood. Nevertheless, there are important lessons to be learned from the past in order to develop strategies to achieve a desirable hydrogen store, making full use of ceramic (nano-) particles, clusters and carbon. This review focuses on some fundamental achievements in the pursuit of hydrogen storage materials, particularly based on hydride systems.

2. Technical challenges for hydrogen storage

The "grand challenge" in identifying an ideal hydrogen storage system is to meet simultaneously all the targets for practical on-board vehicular applications (Fig. 1). These targets or required properties are closely associated with three sets of parameters: structure (crystalline form, specific surface area or particle size, and structural defects), chemistry (components, composition, phases, catalysts, and impurities), and reaction or diffusion path (elementary reactions, transient species, . . . , etc.).

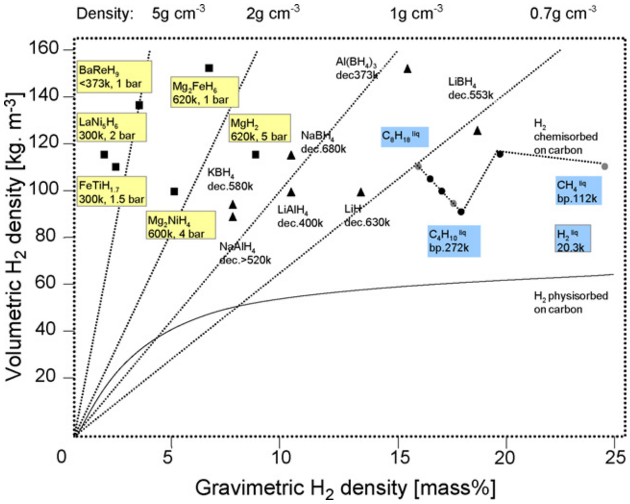

Fig. 2. Volumetric and gravimetric capacities of selected hydrogen storage materials[16].

These are interacting and the critical issues differ for different types of hydrogen storage materials.

2.1. Capacity

Most metallic elements can form hydrides at various conditions, with relatively strong chemical bonding. However, the requirement for a high system storage capacity of more than 6 mass% immediately eliminates hydride systems beyond the first 20 elements in the Periodic Table, primarily leaving us with Li, B, Na, Mg, Al, N and C when other chemical characteristics of the elements are taken into consideration. Several promising hydrogen storage systems, based on M–H, M–N–H and M–B–H (M = Li, Na, or Mg) or their mixtures, have been under development in the past decade (Fig. 2).[16] When multi-

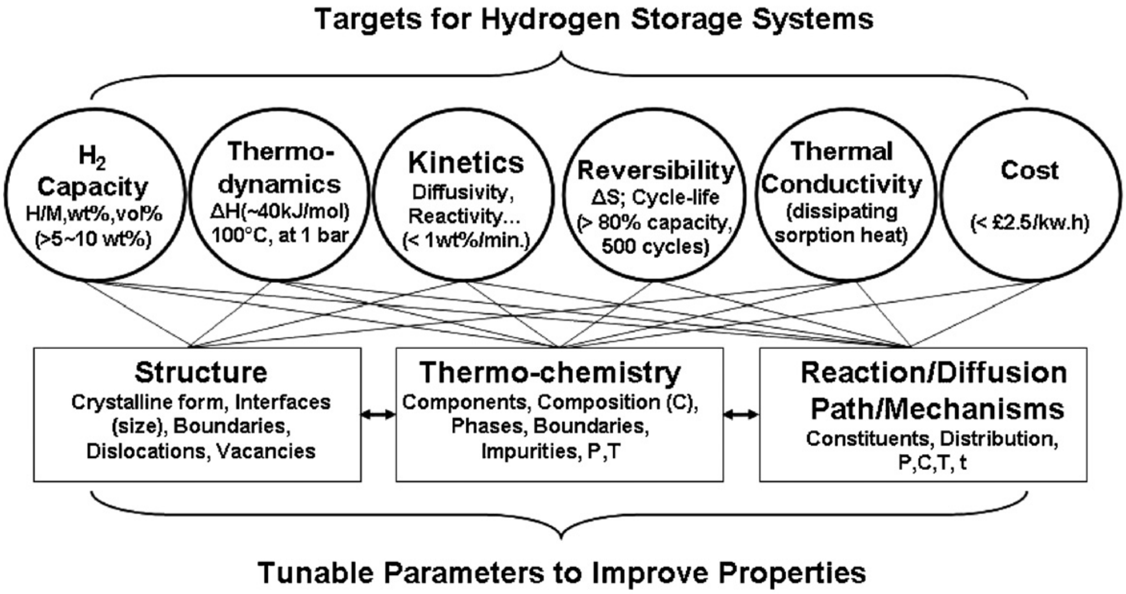

Fig. 1. Practical targets for on-board hydrogen storage in relation to key materials parameters.

component alloys, compounds and polymorphs are counted, there are still a large number of possible candidates that meet the capacity requirement. It is usually the thermodynamic, kinetic and/or reversibility issues that limit their practical applications.

2.2. Thermodynamic stability

Hydrogen may be stored in a system dominated either by chemisorption, e.g. hydrides, or physisorption, e.g. carbon structures, zeolites and metal-organic frameworks (MOFs). The former is usually too strong (>60 kJ/mol H_2) and demand high desorption temperatures to break up the bonds, whereas the latter is too weak (<10 kJ/mol H_2) and requires cryogenic temperatures to achieve a useful capacity. For practical applications, rapid hydrogen desorption is required around 100 °C and one atmospheric pressure, which corresponds to an enthalpy of formation around 15–25 kJ/mol H_2.[16] Hence, an ideal hydrogen storage system is likely to involve hybrid sorption mechanisms and/or reaction paths that can result in an effective enthalpy change lower than that of simple chemisorption but much higher than that of physisorption. Design from electronic structures offer the possibility of identifying some promising candidates.[17,18]

2.3. Kinetics

Hydrogen needs to be supplied at a sufficiently high rate to a fuel cell in order to accelerate a car and then maintain it at a desirable speed. A relatively high hydrogen desorption rate is thus required (rapid rate for absorption is also required for rapid charging). Hydrogen desorption actually involves multi-steps: de-bonding from host atoms, diffusion in a host structure, diffusion to/along surfaces, formation of hydrogen molecules and dissociation from the surface of the material (the reverse occurs in absorption). The slowest step determines the overall kinetics of sorption. It is usually difficult but important to pin point which step is rate controlling in hydrogen sorption. Particle refinement/activation and catalysis to reduce energy barriers for hydrogen diffusion or molecule formation/dissociation are common approaches to enhance the overall kinetics.

2.4. Reversibility

Thermodynamic reversibility is an ideal concept, where a process is said to be “reversible” if it can be reversed by infinitesimal changes of a property without causing any loss or dissipation of energy, i.e. the total entropy change is zero. In theory, all processes are reversible. In practice, good reversibility is only obtained if comparable forward and reverse reactions fall well within practically achievable conditions, e.g. temperature, pressure, and kinetics. This effectively means that the rate-controlling energy barriers for the forward and reverse processes (reactions) should be relatively small and of similar values.

Practical reversibility in hydrogen storage materials is usually referred to as the easiness of reversing the hydriding and dehydriding process around service conditions (a few hundred degrees of temperature and tens of atmospheric pressure). There will be energy input or entropy increase in either direction to achieve a practically useful rate of reaction. This can be limited either thermodynamically by the stability of a hydride, e.g. complex chemical hydrides with relatively strong chemical bonding, or kinetically by the rate-controlling energy barrier, e.g. in a simple hydride. Sometimes, indirect reversibility can be achieved by following multi-step/different reaction paths in the case of reactive hydrogen sorption between two or more species.

2.5. Thermal conductivity and cost

Hydrides are poor thermal conductors with relatively high enthalpies of formation. The desorption reaction is usually endothermic and absorption exothermic. This means that considerable amount of reaction heat needs to be dissipated during hydrogen charging (absorption), and heating is needed for hydrogen desorption. Highly conductive cooling/heating structures are necessary in the design of a hydrogen storage system.

Cost is an important issue in all technologies. For hydrogen and fuel cells to be adopted in practice, it is important that the cost of running on hydrogen is competitive with that of running on petroleum, in the case of domestic transport.

3. Structural modifications by mechanical milling

Mechanical milling relies on mechanical impact and friction to refine and/or alloy powder materials. Mechanical alloying of different types of powder mixtures is able to produce supersaturated solid solutions, amorphous alloys, intermediate phases and nanocrystalline materials. Both thermodynamic and kinetic effects can be imparted from the process, while chemical additives can be applied to enhance such effects.

Mechanical milling can lead to thermodynamic changes by the introduction of substantial levels of relatively stable structural defects, phase change and/or crystallinity.[19,20] A heavily defected or amorphous structure possesses different hydriding characteristics from the crystalline counterpart, although both materials may have identical chemical composition. Usually, hydrogen atoms occupy similar interstitial sites in the amorphous structure to those in the crystalline counterpart, but the binding energy of the interstitial site varies, due to heavy and varied lattice distortion in the former. Therefore, a metastable configuration leads to a certain level of shift in the plateau pressure, even the absence of a plateau in the pressure–composition isotherms (P–C–T curves), and so further extends the limits of solid solubility of hydrogen in metals. An example of such changes is presented in Fig. 3 for FeTi, where the pressure plateau totally disappears for the amorphous case.[21] Though the hydrogen storage capacity is relatively low in this compound, it can absorb/desorb hydrogen around ambient conditions.

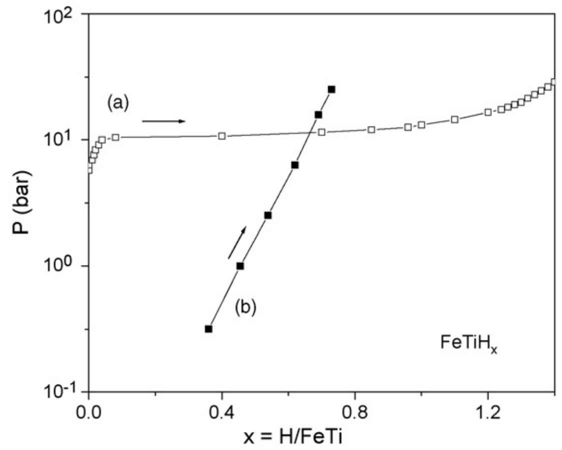

Fig. 3. Pressure–composition isotherms of absorption at room temperature for: (a) polycrystalline FeTi and (b) amorphous FeTi[1].

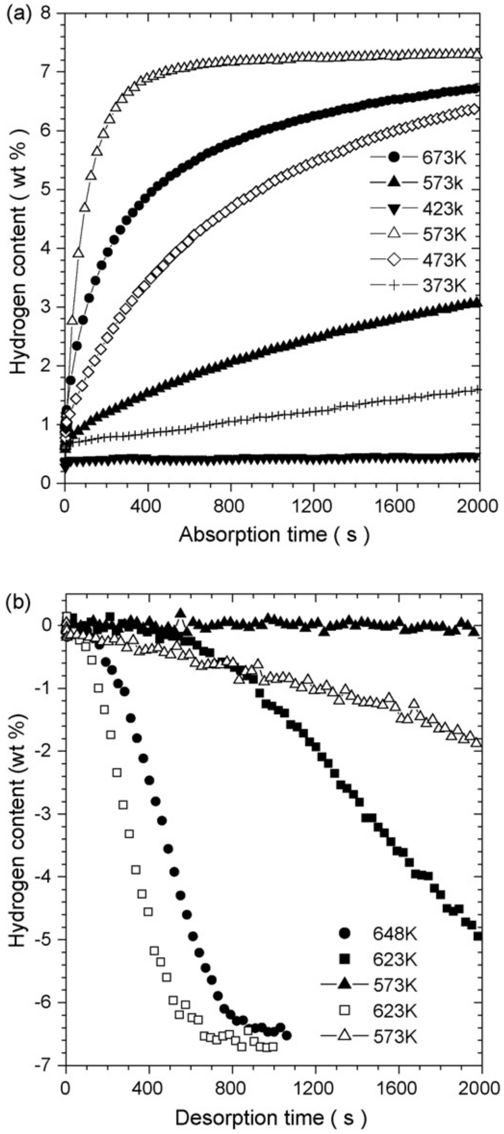

Fig. 4. Hydrogen sorption curves: (a) absorption under 1 MPa hydrogen and (b) desorption under 0.015 MPa hydrogen. Curves of un-milled magnesium (filled marks) and ball-milled magnesium (hollow marks) MgH_2[25].

Kinetic processes at solid surfaces are usually the rate-determining step for the overall hydrogen sorption kinetics. Firstly, metal surfaces are generally covered by a thin layer of oxide, which inhibits the dissociation of hydrogen molecules and the diffusion of atomic hydrogen into the bulk. Secondly, the formation of surface hydrides may create a diffusion barrier blocking further transport of atomic hydrogen into the bulk. The poor hydrogen absorption/desorption kinetics of Mg is typically acknowledged to be the result of the above two phenomena. Magnesium oxide forms readily on Mg surfaces exposed to air. The oxide at the Mg surface plays a dual role. On the one hand, discontinuous oxide of small quantity helps the nucleation of magnesium hydride; on the other, it passivates the metal surface completely when the oxide layer becomes thick and compact. Magnesium hydride grows quickly at the metal surface when hydrogen pressure is well above the equilibrium value, forming a nearly uniform surface hydride layer. The kinetics is eventually limited by the diffusion of hydrogen through this product layer. To avoid the drawbacks of surface passivation of hydrogen–metal systems, an activation process is needed to make the surface reactive again, e.g. by mechanical or chemical (etching) surface cleaning to break or remove the oxide layer at room temperature.

4. Modifications by chemical additions

4.1. MgH_2

Among all the metal hydrides, Mg has been the one mostly studied because of its relatively large hydrogen storage capacity (7.6 mass%) and low cost. However, its hydriding and dehydriding kinetics are very slow and dehydrogenation does not occur below 300 °C due the high energy required ($\Delta H = -75$ kJ/mol).[22] Magnesium has been alloyed with metals such as Cu, La and Fe.[22,23] Transition metal catalysts such as Pd or Pt have also been added to magnesium to facilitate the dissociation and recombination of hydrogen molecules at the surface of magnesium particles.[24] The hydriding and dehydriding reactions of Mg are controlled by nucleation and growth of the hydride phase or magnesium phase, respectively.

A real breakthrough was achieved when the crystallite of magnesium was reduced to the nanometer range by high energy ball milling MgH_2 (Fig. 4).[25] Further improvement was obtained by mechanically milling magnesium hydride with transition metals or metal oxides.[26,27] Klassen and coworkers showed that hydrogen could be released from metal oxides milled with nanocrystalline Mg-based hydrides at temperature as low as 250 °C in less than an hour.[28] Of all the different oxides, i.e. Nb_2O_5, TiO_2, V_2O_5, Cr_2O_3, Mn_2O_3, Fe_3O_4, CuO, and Nb_2O_5 leads to the most improved kinetics. The real effects of these metal oxides on the kinetic properties of MgH_2 are not known. It is believed that these catalyse the reaction of hydrogen dissociation and recombination at the surface of the magnesium particles and thus accelerate the gas–solid reaction.

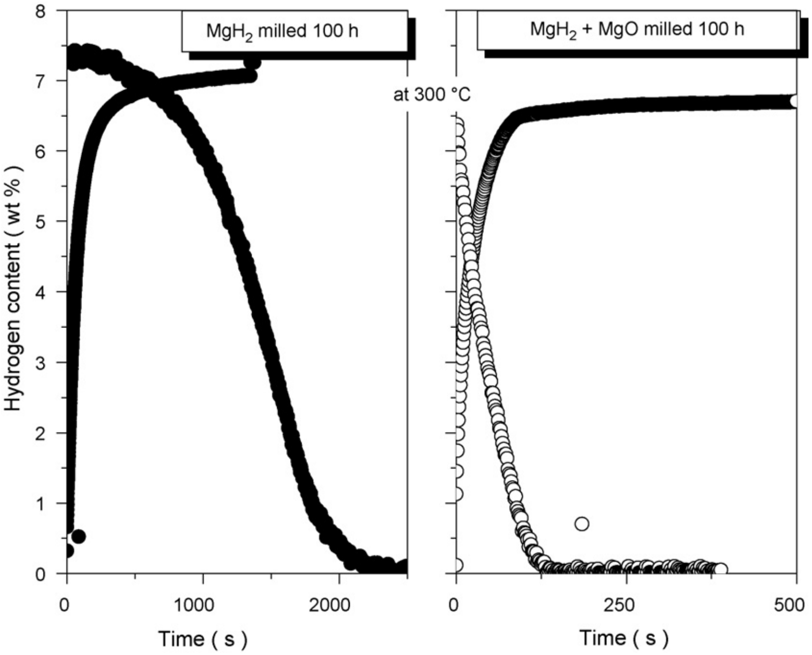

Fig. 5. Hydrogen sorption curves for MgH_2 milled with and without MgO[29].

However, several reports mentioned the role of metal oxides in facilitating the refinement of MgH_2 particle size during milling. Metal oxides could prevent MgH_2 particle agglomeration during mechanical milling, which also favours the synthesis of small magnesium hydride particles. Smaller particles absorb hydrogen more rapidly because diffusion paths are shorter and there are more surfaces for hydrogen to interact.

Aguey-Zinsou and coworkers used MgO to demonstrate the point of oxide effects.[29] MgH_2 milled with MgO leads to a material that shows hydrogen sorption kinetics as good as those modified by transition metals (Fig. 5). In addition, it has been reported that using oxides with a strong ionic character (polar-oxides), such as Al_2O_3 and TiO_2, reduces the problem of agglomeration during mechanical milling, as compared with metal oxides with a weak ionic character (near covalent bond), such as SiO_2. Furthermore, during cycling, the presence of the metal oxides could prevent sintering of the magnesium particles.

4.2. *Complex hydrides*

Some of the lightest metals in the periodic table, such as Li, B, Na and Al, form stable and ionic compounds with hydrogen. In addition, the hydrogen content of these complex hydrides can reach 18 mass% for $LiBH_4$ and hydrogen release can occur at temperatures as low as 150 °C for $LiAlH_4$. However, for most of the complex hydrides the dehydrogenation reaction is not reversible under proposed service conditions because of the segregation of the different components. To achieve a good reversibility, high temperatures and pressures are required. Since Bogdanović and Schwickardi showed reversible hydrogenation of $NaAlH_4$, as a result of the addition of titanium chloride, around 150 °C and at a moderate pressure,[30] there have been many studies on the modification of hydrogenation properties of complex hydrides with transition metal-based compounds, such as oxides and halides.[31] The exact effect of titanium doping is not clear but it is believed that titanium induces distortions in the lattice of $NaAlH_4$ which facilitate the hydrogenation reaction.

Züttel et al. have also shown that the decomposition temperature of $LiBH_4$ could be brought down from 600 to 400 °C by the addition of SiO_2[32] It is believed that SiO_2 increases the surface

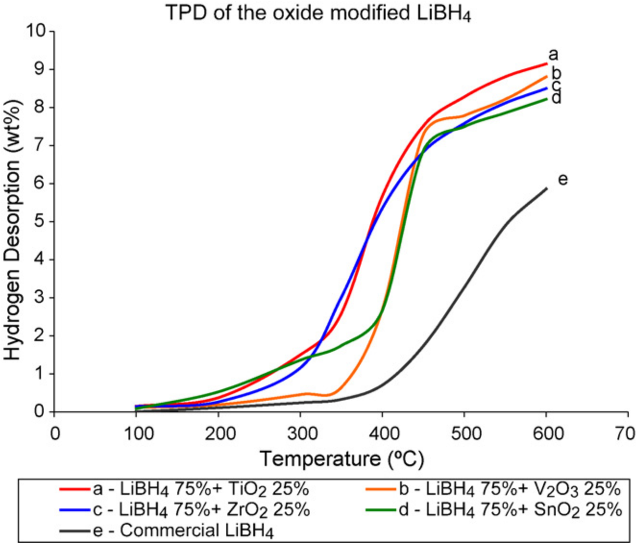

Fig. 6. Comparison of hydrogen desorption properties of modified $LiBH_4$ materials with a commercial $LiBH_4$[32].

area of the molten borohydride and therefore enhances the dehydrogenation kinetics. Other metal oxides can also been used to improve the decomposition of $LiBH_4$ as shown Fig. 6. Metal oxides have also been added to amide systems. However, these did not have any significant effect on the hydrogen kinetics of the $LiNH_2$–LiH system.[33] Further improvement of $LiNH_2$–LiH hydrogen kinetics was obtained by using nitrides facilitating the diffusion of lithium ions during the solid state reaction of $LiNH_2$ with LiH.[33]

It appears that the effects of metal oxides vary, depending on the hydride system. While metal oxide additives may enhance the hydrogen kinetics of magnesium, for complex hydrides metal oxide addition is not always successful. Hydrogenation and dehydrogenation of complex hydrides involves relatively complex multi-step mechanisms as compared to metal hydrides. It is difficult to enhance all the steps at once with a single dopant. Engineering a particular reaction step or path may prove very effective in the practical development of hydrogen storage materials.

5. Conclusions

Critical challenges for the development of hydrogen storage materials are systematically addressed. The important roles of mechanical milling and chemical doping in modifying hydride properties are discussed. The effects of oxide additives on hydrogen kinetics of MgH_2 and complex hydrides were compared. It is clear that for automobile applications, the progresses so far are insufficient to meet all the practical targets for on-board hydrogen storage. The dehydrogenation and hydrogenation of hydride materials still require high temperatures. With compute-guided materials design, hybrid and reactive couples may lead to new hydrogen storage systems that meet the technical requirements.

Acknowledgements

This project is financially supported by the EPSRC SUPERGEN Initiative under the UK Sustainable Hydrogen Energy Consortium (UK–SHEC: GR/S26965/01, EP/E040071/1), the EPSRC Grant (EP/E037267/1) and a Platform grant (EP/E046193/1).

References

1. Metz, B., *Intergovernmental Panel on Climate Change: Special Report on CO_2 Capture and Storage*, October 2005.
2. Raupach, M. R., Marland, G., Clais, P., Le Quere, C., Canadell, J. G., Klepper, G. and Field, C. B., *PNAS*, 2007, **104**(24), 10288–10293.
3. World Energy Technology Outlook 2050, European Commission, 2006.
4. Shang, C. X. and Guo, Z. X., Effect of carbon on hydrogen desorption and absorption of mechanically milled MgH_2. *J. Power Sources*, 2004, **129**, 73–80.
5. Wronski, Z. S., *Int. Mater. Rev.*, 2001, **46**, 1–49.
6. Percheron-Guegan, A., *Hydrogen in Intermetallic Compounds I.* Springer–Verlag, Heidelberg, 1988 [Chap. 6].
7. Reilly, J. and Wiswall, R. H., Formation and properties of iron titanium hydride. *Inorg. Chem.*, 1974, **13**, 218–222.
8. Tessier, P., *Hydrogen storage in metastable Fe–Ti*, PhD thesis, McGill University, Montreal, Canada, 1995.
9. Zaluska, L., Zaluska, A. and Ström-Olsen, J. O., Hydrogen absorption in nanocrystalline Mg_2Ni formed by mechanical alloying. *J. Alloys Compds.*, 1995, **217**, 245–249.
10. Yamamoto, K., Tanioka, S., Tsushio, Y., Shimizu, T., Morishita, T., Orimo, S. and Fujii, H., Influence of elemental diffusion on low temperature formation of MgH_2 in $TiMn_{1.3}T_{0.2}$-Mg (T = 3d-transition elements). *J. Alloys Compds.*, 1996, **243**, 144–150.
11. Bogdanović, B. and Schwickardi, M., Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials. *J. Alloys Compds.*, 1997, **253**, 1–9.
12. Zaluska, A., Zaluska, L. and Ström-Olsen, J. O., Sodium alanates for reversible hydrogen storage. *J. Alloys Compds.*, 2000, **298**, 125–134.
13. Tang, C., Bando, Y., Ding, X. and Qi, S., Catalyzed collapse and enhanced hydrogen storage of BN nanotubes. *J. Am. Chem. Soc.*, 2002, **124**, 14550–14551.
14. Dillon, A. C., Jones, K. M., Bekkedahl, T. A., Kiang, C. H., Bethune, D. S. and Heben, M. J., Storage of hydrogen in single-walled carbon nanotubes. *Nature*, 1999, **386**, 377–379.
15. Chen, P., Xiong, Z., Luo, J., Lin, J. and Tan, K. L., Interaction of hydrogen with metal nitrides and imides. *Nature*, 2002, **420**, 302–304.
16. Schapbach, L. and Züttel, A., Hydrogen-storage materials for mobile applications. *Nature*, 2001, **414**, 353–358.
17. Shevlin, S. A. and Guo, Z. X., Hydrogen sorption in defective hexagonal BN sheets and BN nanotubes. *Phys. Rev. B*, 2007, **76**, 024104–024115.
18. Song, Y. and Guo, Z. X., Electronic structure, stability and bonding of the Li–N–H hydrogen storage system. *Phys. Rev. B*, 2006, **74**, 195120–195127.
19. Berube, V., Radtke, G., Dresselhaus, M. and Chen, G., Size effects on the hydrogen storage properties of nanostructured metal hydrides: a review. *Int. J. Energy Res.*, 2007, **31**, 637–663.
20. Shang, C. and Guo, Z. X., *Int. J. Hydrogen Energy*, 2007, **32**, 2920–2925.
21. Zaluski, L., Tessier, P., Ryan, D. H., Doner, C. B., Zaluska, A., Ström-Olsen, J. O., Trudeau, M. L. and Schulz, R., Amorphous and nanocrystalline Fe–Ti prepared by ball milling. *J. Mater. Res.*, 1993, **8**, 3059–3068.
22. Shang, C. X., Bououdina, M., Song, Y. and Guo, Z. X., Mechanical alloying and electronic simulations of ($MgH_2 + M$) systems (M = Al, Ti, Fe, Ni, Cu and Nb) for hydrogen storage. *Int. J. Hydrogen Energy*, 2004, **29**, 73–80.
23. Akiba, E., Nomura, K. and Ono, S., Kinetics of the reaction between Mg–23.3% Ni eutectic alloy and hydrogen. *J. Less-Common Met.*, 1983, **89**(1), 145–150.
24. Eisenberg, F. G., Zagnoli, D. A. and Sheridan, J. J., The effect of surface nickel on the hydriding–dehydriding kinetics of MgH_2. *J. Less-Common Met.*, 1980, **74**, 323–331.
25. Huot, J., Liang, G., Boily, S., Van Neste, A. and Schulz, R., Structural study and hydrogen sorption kinetics of ball-milled magnesium hydride. *J. Alloys Compds.*, 1999, **293–295**, 495–500.
26. Song, M., Bobet, J. and Darriet, B., Improvement in hydrogen sorption properties of Mg by reactive mechanical grinding with Cr_2O_3, Al_2O_3 and CeO_2. *J. Alloys Compds.*, 2002, **340**, 256–262.
27. Oelerich, W., Klassen, T. and Bormann, R., Metal oxides as catalysts for improved hydrogen sorption in nanocrystalline Mg-based materials. *J. Alloys Compds.*, 2001, **315**, 237–242.
28. Aguey Zinsou, K. F., Ares-Fernandez, J. R., Klassen, T. and Bormann, R., Using MgO to improve the (de)hydriding properties of magnesium. *Mater. Res. Bull.*, 2006, **41**, 1118–1126.
29. Ares-Fernandez, J. R., Aguey-Zinsou, K. F., Klassen, T. and Bormann, R., Influence of impurities on the milling process of MgH_2. *J. Alloys Compds.*, 2007, **434–435**, 729–733.
30. Bogdanović, B. and Schwickardi, M., Ti-doped $NaAlH_4$ as a hydrogen-storage material-preparation by Ti-catalyzed hydrogenation of aluminum

powder in conjunction with sodium hydride. *Appl. Phys. A*, 2001, **72**, 221–223.

31. Ares-Fernandez, J. R., Aguey-Zinsou, K. F., Elsaesser, M., Ma, X. Z., Dornheim, M., Klassen, T. and Bormann, R., Mechanical and thermal decomposition of $LiAlH_4$ with metal halides. *Int. J. Hydrogen Energy*, 2007, **32**(8), 1033–1040.
32. Züttel, A., Wenger, P., Rentsch, S., Sudan, P., Mauron, Ph. and Emmenegger, Ch., $LiBH_4$ a new hydrogen storage material. *J. Power Sources*, 2003, **118**(1–2), 1–7.
33. Yao, J. H., Shang, C., Aguey Zinsou, K. F. and Guo, Z. X., Desorption characteristics of mechanically and chemically modified $LiNH_2$ and $(LiNH_2 + LiH)$. *J. Alloys Compds.*, 2007, **432**, 277–282.