# AxBy Intermetallics for hydrogen storage

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AxBy intermetallics show outstanding performances, notably for stationary hydrogen storage applications. Elemental substitution, whether on the A or B site of these alloys, allows the effective tailoring of key properties such as gravimetric density, equilibrium pressure, hysteresis and cyclic stability for instance.

## 1. Introduction

Humankind is on the verge of facing a worldwide energy crisis considering the soon-to-come fossil fuels shortage. The transition to environmentally friendly energy sources is a challenge that many countries are already tackling by reformatting their economy to implement alternative and sustainable solutions. As such, the hydrogen-based economy became one of the main candidates for the transition towards cleaner energy source, in the light of hydrogen's positive impact on the environment and its intrinsic great potential as an abundant energy carrier: (i) high gravimetric energy density of 142 MJ kg$^{-1}$ (against only 47 MJ kg$^{-1}$ for petroleum) and (ii) high energy efficiency (fuel cells electrochemical processes show ~50–60% efficiency whereas that of combustion engines is as low as 25% for hydrogen-air mixtures, but still slightly higher than petrol-air) [1].

The main requirements for a large scale application of metal hydrides for on-board applications are (i) low hydrogen release temperature in the typical working conditions of a PEM fuel cell, (ii) high hydrogen absorption and desorption rates, (iii) acceptable costs and most importantly (iv) high storage capacity of 8 wt% according to the recent European VII FP call [2], which sets the bar even higher than the 6 wt% targeted by the American Department of Energy (DOE) [3]. It is difficult to achieve the gravimetric capacity target, especially for intermetallic hydrides. Hence, the main application for the intermetallic hydrides would be stationary applications, which are essential parts of renewable energy systems.

## 2. AB$_5$-Type Alloys

The AB$_5$-type hydrides have been intensively studied during the last decades for their high potential for practical applications [4]. They have reversible and fast hydrogen absorption/desorption kinetics at near-ambient temperatures, simple activation process, and moderate pressure-temperature conditions of hydrogenation/dehydrogenation, which can easily be controlled. However, the maximum discharge capacity is limited to only around 1.5 wt% for the single CaCu$_5$-type hexagonal structure [5][6].

In this section, LaNi$_5$ is taken as the reference material of the AB$_5$ family, in the light of its remarkable properties and features in comparison with other AB$_5$ compounds that were recently studied. Indeed, LaNi$_5$-based hydrides show good hydrogen absorption/desorption characteristics under near-atmospheric conditions and excellent kinetics [7][8]. The amount of hydrogen desorbed from a typical LaNi$_5$-type metal-hydride system ranges from much less than 1 wt% up to 1.2 wt% H$_2$ between room temperature and 373 K, with a theoretical maximum reversible storage capacity of 1.5 wt% H$_2$ (still below the DOE's target) [9]. Despite attractive properties, LaNi$_5$-based compounds have a high cost in comparison with other alloys and show a significant capacity loss (higher than 30% after 800 cycles under impure hydrogen gas containing 100 ppm of O$_2$ [10]), therefore urging to develop other materials with higher discharge capacity, better cyclic stability and lower cost [11].

The costly lanthanum in LaNi$_5$ can thus be replaced by cheaper rare earth elements such as Ce [12], or by a cheaper rare earth mixture called mischmetal (Mm) consisting of La, Ce, Pr and Nd [13], which was investigated in many studies. MmNi$_5$ possesses a hexagonal crystal structure similar to that of LaNi$_5$ and tends to form stable hydrides. However, it shows a very high activation pressure (120 atm at 298 K), a high hydride formation pressure (30–60 atm at 298 K), large hysteresis

between the absorption and desorption pressures and a maximum storage capacity of about 20% lower than that of LaNi$_5$ [14][15]. Many groups have attempted to reduce the high hydride formation pressure in MmNi$_5$ by partially substituting A and B components with various elements [16][17][18].

To enhance the hydrogen storage capacity, Ca may partially replace Mm in MmNi$_5$ because of its lightweight (at. wt. 40) in comparison to Mm (at. wt. 140, corresponding to the following composition: La 22%, Ce 52%, Nd 15% and Pr 11%). Hence, for H/M = 1.0 the storage capacity of MmNi$_5$H$_6$ is 1.38 wt%, while that of Mm$_{0.66}$Ca$_{0.34}$Ni$_5$H$_6$ corresponds to 1.5 wt% [19][20]. The studies on Mm$_{1-x}$Ca$_x$Ni$_5$ were first reported by Sandrock [21] and Shinar et al. [22]. Sandrock's results show that the hydride dissociation pressure decreased with increasing Ca content, while Shinar's results indicate that the substitution of Ca for Mm or La caused an increase in hydride dissociation pressure. Such contradictory behaviour results from the variation in Ca content, as elucidated by Wang et al. [23]. Indeed, they reported that the dissociation pressure of the hydrides (at 298 K) increased when x < 0.3 but decreased when 0.3 < × < 0.9, which was attributed to the effect of geometrical and electronic factors. In addition, the first hydrogenation incubation time shortened and its absorption rate increased along with increasing x in Mm$_{1-x}$Ca$_x$Ni$_5$, and the hysteresis reduced.

Different from Mm and Ca (A substitutes), substitutions for B element were reported to be effective in tailoring the plateau pressure. Among them, Al was used for reducing the plateau pressure, for instance from 50 atm for MmNi$_5$ down to 0.5 atm for MmNi$_{4.2}$Al$_{0.8}$. However, the maximum storage capacity decreased from 1.44 to 1.3 wt% and the plateau slope increased [24]. Meanwhile, Fe is known to increase hydrogen storage capacity (1.5 wt% for MmNi$_{4.6}$Fe$_{0.4}$), and reduce sloping and hysteresis [25][26].

## 3. AB$_2$-Type Alloys

AB$_2$ Laves phase is another type of alloy with high potential for hydrogen storage. Usually, these alloys exist in three different crystal structures: cubic C15 (for instance MgCu$_2$, ZrV$_2$), hexagonal C14 (MgZn$_2$, ZrMn$_2$) and double hexagonal C36 (MgNi$_2$). Laves phases with A = Zr show relatively high capacities (ZrV$_2$H$_{5.3}$, ZrMn$_2$H$_{3.6}$, ZrCr$_2$H$_{3.4}$), faster kinetics, longer lifetime and a relatively low cost in comparison to the LaNi$_5$-based alloys. However, their hydrides are too stable at room temperature and more sensitive to contaminants [27]. This high stability of Zr-containing alloys is also seen in various type of materials, notably in amorphous structures in which hydrogen is irreversibly immobilized either in trapping sites [28][29][30], or by forming stable ZrH$_2$ phase [31][32].

In this section, we take Ti–Mn Laves phase alloys as the reference material of the AB$_2$ family, because of their easy activation, good hydriding-dehydriding kinetics, high hydrogen storage capacity and relatively low cost. Besides, they display high plateau pressure at room temperature (over 20 atm) and a sloping plateau often accompanied with a large hysteresis that requires major improvements [33][34].

In 2005, Toyota's group demonstrated the use of Ti$_{1.1}$MnCr alloys in a high-pressure metal hydride (MH) tank. This alloy has a maximum storage capacity of 1.9 wt%, but it has been reached only for a hydrogen pressure of around 350 atm at room temperature [35]. Kandavel et al. [36] substituted Zr in Ti$_{1.1}$CrMn to provide favorable hydrogen sorption conditions and maximize the storage capacity. The increase in Zr content leads to a decrease in the equilibrium plateau pressure and faster absorption kinetics, together with an increase in the hydrogen storage capacity from 1.9 to 2.2 wt% for Ti$_{1.1}$CrMn and (Ti$_{0.9}$Zr$_{0.1}$)$_{1.1}$CrMn, respectively. Besides, Park et al. [37] conducted studies on Ti–Zr–Mn–Cr based metal hydrides and concluded that when Zr/Ti ratio increases, the lattice strain increases. This is partially responsible for a drastic increase of sloping, while the use of Cu was found very effective to mitigate the sloping.

In 1995, Morii et al. [38] prepared and investigated (Ti, Zr)(Ni, Mn, X)$_2$ alloys, where X is V or/and Fe. The results showed that V lowers both hysteresis and plateau pressure. On the other hand, Ni raises the plateau pressure and reduces the width of the plateau region, while Fe flattens and lengthens it.

Improvements of the hydrogen storage properties of Laves phase AB$_2$-type alloys at 303–308 K and 1–15 atm have been achieved by introducing non-stoichiometry at the A site of (Ti$_{0.65}$Zr$_{0.35}$)$_{1+x}$MnCr$_{0.8}$Fe$_{0.2}$ alloys. From pressure-composition-temperature (PCT) measurements, the maximum hydrogen storage capacity was found to be around 2.2 wt% at 35 atm and 305 K for (Ti$_{0.65}$Zr$_{0.35}$)$_{1.1}$MnCr$_{0.8}$Fe$_{0.2}$, which is approximately 16% higher than that of the commercially available "Hydralloy C5" (Ti$_{0.955}$Zr$_{0.045}$Mn$_{1.52}$V$_{0.43}$Fe$_{0.12}$Al$_{0.03}$). These alloys show remarkable hydrogenation kinetics: the full capacity is reached within 10 min without any need for activation [39].

Alloys without zirconium (such as Ti$_{1.02}$Cr$_{1.0}$Fe$_{0.75}$Mn$_{0.25}$) display 1.55 wt% of reversible hydrogen storage capacity when the temperature is as low as 233 K. However, without zirconium the effective hydrogen capacity is optimal only when the pressure is higher than 70 atm [40], proving the effectiveness of Zr in Laves phase alloys.

Recent developments (<5 years) on $AB_2$-type materials have highlighted their significant potential for high-pressure compressors, notably (Ti,Zr)(Mn,Cr)-based alloys. Indeed, Corgnale et al. [41] proposed a techno-economic analysis of metal hydride systems for efficient and novel high-pressure compressors. Among various materials, $TiCr_{1.9}$, $Ti_{1.1}CrMn$, $TiCrMn_{0.4}Fe_{0.4}V_{0.2}$, and $(Ti_{0.97}Zr_{0.03})_{1.1}Cr_{1.6}Mn_{0.4}$, they suggested the last one as the best candidate for their novel two-stage hybrid electrochemical and metal hydride compression system, since pressures about 863 atm can be reached with a thermal power provided at approximately 423 K.

Pickering et al. [42] further demonstrated the high capability of (Ti,Zr)(Mn,Cr)-based alloys for both hydrogen storage and high-pressure compression by producing industrial volumes (~10 kg) of tailored $AB_2$ intermetallics (A = Ti + Zr, B = Cr + Mn + Ni+Fe + V) by means of vacuum induction melting process. They successfully tuned the hydrogenation properties of the alloy, showing that at a fixed quite low Zr/(Ti + Zr) ratio the PCT properties of the materials can be adjusted in a wide range by the variation of V content which, in addition, results in the increase of the hydrogen storage capacity. Cheaper alternatives to pristine Ti and V nevertheless exist, notably by replacing those high purity raw materials by their low-cost and low-purity counterparts, namely Ti sponge and ferrovanadium (FeV), respectively. Such substitution in (Ti,Zr)(V,Fe,Cr,Mn) reduces the raw material cost by 83%, without altering the dissociation pressure (15 atm), nor the reversibility (1.4 and 1.5 wt% $H_2$ after 1000 cycles, against an initial capacity of 2 and 1.7 wt% $H_2$ for pristine and modified alloys, respectively) [43].

The development of hybrid hydrogen storage system is equally appealing to the scientific community. For instance, rare earth elements (RE) such as La, Ce or Ho in $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}RE_{0.03}$ have been shown in 2018 to yield better activation behaviour, larger storage capacity but lower desorption plateau pressure [44]. This study suggests $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}La_{0.03}$ alloy as the best overall candidate since it can be fully activated at room temperature, and has a hydrogen storage capacity as high as ~1.7 wt%. Another example of hybrid system is reported by Puszkiel et al. [45], who demonstrated that mixing expanded natural graphite (ENS) into $(Ti_{0.9}Zr_{0.1})_{1.25}Cr_{0.85}Mn_{1.1}Mo_{0.05}$ alloy not only improves the heat transfer properties, but also yields a reversible capacity of about 1.5 wt%, together with decent cycling stability and rapid reaction kinetics (25 to 70 s).

Although all the above-mentioned (Ti,Zr)(Mn,Cr)-based Laves phase alloys are widely investigated in the light of their superior potential for high-pressure compressors (and hybrid hydrogen storage), Zr-based $AB_2$ materials are nevertheless not to be discarded although they display significantly lower desorption plateau pressures. Wu et al. [46] thus elucidated the role of Ni addition on the hydrogen storage characteristics of $Zr(V_{1-x}Ni_x)_2$ (x = 0.02, 0.05, 0.1, 0.15, 0.25) intermetallic compounds. The hydrogen absorption capacity turns out to decrease, and the equilibrium pressure increases with increasing Ni content. The alloys exhibit fast absorption kinetics at room temperature and a remarkable cyclic stability even after 100 hydrogen absorption/desorption cycles.

Owing to fast kinetics, high equilibrium pressure and impressive volumetric hydrogen storage density at ambient temperature, $ZrFe_2$ based alloys are similarly good candidates for high pressure compressed hydrogen tanks. To bypass its rather large hysteresis, Mn, Ti, V and Cr addition [47][48] has been considered. On one hand, V addition is suggested to improve the hysteresis, while Ti helps to lower plateau sloping as well as to increase the plateau pressure. $Zr_{1.05}Fe_{1.6}Mn_{0.4}$ shows a relatively high dehydriding pressure of 20.6 atm at 298 K, while $(Zr_{0.5}Ti_{0.5})_{1.05}Fe_{0.95}MnV_{0.05}$ delivers a maximum capacity of 1.64 wt% $H_2$ and shows a dehydriding pressure of 6.8 atm at 298 K (calculated from Van't Hoff plots) [49]. Additionally, the simultaneous Cr/V substitution for Fe decreases the equilibrium pressure (due to the enlarged unit cell), and $Zr_{1.05}Fe_{1.85}Cr_{0.075}V_{0.075}$ seems to exhibit decent overall hydrogen storage properties (1.54 wt%, and a desorption equilibrium pressure of 9.7 atm at 243 K) [50].

## 4. AB-Type Alloys

AB-type alloys are attractive materials for hydrogen storage because of their light molar mass and high weight capacities. TiFe alloys with cubic CsCl-type structures are the most known alloys of this class and stand among the best hydrogen storage materials up to this date [51].

TiFe intermetallic compound is one of the most promising hydrogen storage alloys, due to its relatively high theoretical hydrogen storage capacity (1.9 wt%) at near-ambient conditions compared to other $A_xB_y$ families. Besides, its economical merit based on the abundance and low cost of the constituting elements encourages extensive investigations on the TiFe system.

The hydrogen sorption and desorption in TiFe was first described by Reilly and Wiswall in the year 1974 [52]. They reported two stable intermetallics of TiFe system (TiFe and $TiFe_2$) and a third, $Ti_2Fe$ that forms only above 1273 K (dissociates to TiFe and Ti below that temperature). Only TiFe is known to make two ternary hydrides, TiFeH and $TiFeH_2$.

The hydrogen absorption in TiFe alloy depends on two factors: (i) the Fe/Ti ratio and (ii) the oxygen amount in the alloy. TiFe intermetallic exists over a narrow composition range of ~2.5 at% (from 49.5 to 52 at% Ti). Slightly less than 49.5 at% Ti results in a two-phase mixture of $TiFe_2$ and TiFe, the first being of no use since it is a non-hydride former. If Ti content is higher than 52 at%, the alloy consists of TiFe and (α or β) Ti solid solution [52]. Although Ti itself readily forms hydrides, they are highly stable and are non-reversible at the temperatures of interest (ambient).

The lower plateau level and general shape of the curve is not significantly affected but the maximum hydrogen storage capacity substantially reduces with the increase in oxygen content [53]. Additionally, TiFe usually requires heating over 573 K for activation, which again suggests the low poisoning tolerance resulting in significant deterioration of hydrogen sorption even for trace amounts of gas species (oxygen and water vapor for instance) [54][55]. Most importantly, surface oxidation issues induce significant difficulties notably in the first hydrogenation. The problem with first activation can be resolved by partial replacement of the base element [56][57][58][59][60][61], mechanical alloying [62][63], surface modifications [64], groove rolling and high-pressure torsion [65]. Most of these studies did not lead to an improvement in hydrogen storage properties, and the result was usually a decreased maximum hydrogen absorption capacity and increased desorption temperature of the intermetallic hydrides.

Very recently, in the year 2020, Yang et al. [66], documented the effect of Cr, Mn and Y substitution for Fe on the hydrogen storage properties. They concluded that Cr substituted alloys ($TiFe_{0.9}Cr_{0.1}$, $TiFe_{0.9}Cr_{0.1}Y_{0.05}$) have lower equilibrium pressure and sloped plateaus, thus providing better hydrogenation kinetics as compared to Mn substituted alloys ($TiFe_{0.9}Mn_{0.1}$, $TiFe_{0.9}Mn_{0.1}Y_{0.05}$), which have higher equilibrium pressure but flat plateaus and thus better dehydrogenation kinetics. Y substitution in Ti–Fe–Mn and Ti–Fe–Cr based alloys resulted in αY phase, which transforms to $YH_3$ during hydrogenation.

Ha et al. [67] investigated the contrast in the microstructure of as cast and heat treated TiFe-6 wt% $ZrCr_2$ alloys. They reported that the as cast alloy has 65 wt% TiFe and 35 wt% $TiFe_2$ (C14 Laves phase) while the heat-treated alloy has a portion of $TiFe_2$ transformed to TiFe phase (84 wt%). The activation profile reveals that both the alloys can be activated at room temperature under 30.6 atm $H_2$ but the as cast alloy displays enhanced absorption kinetics (activation starts without any delay while its heat-treated counterpart requires 40 h of incubation time). Both specimens show approximately equal maximum hydrogen storage capacity of 1.7 wt%. The first plateau for the annealed alloy is flatter in shape and the desorption isotherm shows less retained hydrogen as compared to the as cast alloy. In parallel, Jung et al. [68] conducted a study on tailoring the equilibrium plateau pressure of TiFe monohydride and dihydride via V substitution for both Ti and Fe, in order to achieve maximum reversible capacity under a narrow pressure range. When V substitutes for Ti, the monohydride plateau pressure rises whereas a pronounced opposite trend is seen if V substitutes for Fe. Interestingly, the plateau pressure for dihydride is lowered in both the cases.

## 5. $AB_3$-Type Alloys

Research on $AB_3$ alloys, whose structure consist of combined $AB_2$ and $AB_5$ (see equation below), was initially motivated by their strong potential for Ni-MH batteries [69]. Indeed, negative electrode materials based on $AB_3$ can offer a higher hydrogen storage capacity than $AB_5$-types alloys (already commercialized), but unfortunately suffer a severe degradation of their cyclic properties due to pulverization and oxidation/corrosion [70][71].

$$AB_5 + 2(AB_2) = 3(AB_3) \tag{1}$$

Most frequently based on $La_2MgNi_9$, $AB_3$ alloys however turn out to be promising for stationary hydrogen storage applications as well, considering their good activation and hydrogenation/dehydrogenation kinetics on one hand, and their relatively high storage capacity and low cost on the other (thus combining the best features of $AB_5$ and $AB_2$ respectively) [48]. Additionally, the phase composition of $AB_3$ alloys (hence their properties) can be tuned by means of element substitution, heat treatment and different material processing methods, similarly to $AB_2$ alloys [72].

Pioneering work in the seventies [73][74] first reported hydrogen solubility and hydride forming ability of $AB_3$ alloys based on rare earth elements (A side) and transition metals (B side). Later on, Kadir et al. further investigated such alloys, by providing exhaustive reports on the effect of rare earth elements on the hydrogenation properties of $AB_3$ alloys (La, Ce, Pr, Nd, Sm, Gd) [75], as well as on the effect of La and Mg partial replacement by Ca and/or Y in La-Mg-Ni based alloys [76][77].

The hydriding characteristics of $LaNi_3/CaNi_3$ and $RT_3$ phases (R = Dy, Ho, Er, Tb, Gd; T = Fe or Co) showed that the hydrogen storage capacity of the $AB_3$ phases exceeds that of the well-known hydrogen absorber $LaNi_5$ [78]. Due to the special crystal structure of $AB_3$ compounds, it is possible to combine Mg, Ca, and rare earth elements in the A side. Kadir

et al. [79]synthesized $(La_{0.65}Ca_{0.35})(Mg_{1.32}Ca_{0.68})Ni_9$ which absorbs ~1.87 wt% $H_2$ at ~33 atm $H_2$ and 283 K. Under identical pressure condition, Chen et al. [78] reached up to 1.8 wt% $H_2$ at 293 K for $LaCaMgNi_9$.

In order to improve the performance of La–Mg–Ca–Ni $AB_3$-type alloy, Lim et al. investigated the effects of partial substitution with Ce and Al on the hydrogenation properties of $La_{0.65-x}Ce_xCa_{1.03}Mg_{1.32}Ni_{9-y}Al_y$ alloys [80]. Their results indicated that the hydrogen storage capacity significantly decreased after Ce and Al substitution. Xin et al. [81] investigated the effects of Y partial substitution on overall hydrogen storage properties of $(La_{0.65}Ca_{0.35})(Mg_{1.32}Ca_{0.68})Ni_9$. At 1 atm $H_2$, the hydrogen desorption capacity of $La_{0.60}Y_{0.05}Mg_{1.32}Ca_{1.03}Ni_9$ was approximately 1.624, 1.616, and 1.610 wt% at 298, 313, and 333 K, respectively. In addition, the equilibrium pressure could be tailored by altering the Y amount to range 1–10 atm.

The effect of half replacement of Ca by R (R = Nd, Gd and Er) on the phase structure and hydrogen storage property of $Ca_2MgNi_9$ compound was investigated in 2019 by Zang et al. [82]. Results showed that alloys with Gd, Er or Nd instead of La have lower maximum storage capacity (1.4, 1.2, and 1.5 wt% $H_2$, respectively, against 1.87 wt% $H_2$ for La). Desorption behaviours of some remarkable $AB_3$ alloys (plotted in Figure 7) show flatter plateau pressures than some $AB_2$ and AB alloys while displaying comparable storage capacity (see detailed summary in Table 6).

To summarize, partial substitution in the B site of Ni for elements with larger atomic radius increases the unit cell volume and results in a decrease of the absorption and desorption plateau pressures. As such, increasing Co concentration (in $La_{0.7}Mg_{0.3}Ni_{3.4-x}Mn_{0.1}Co_x$ [83] or in $La_2Mg(Ni_{1-x}Co_x)_9$ (x = 0.1–0.5) [84]), or Al and Mo (in $La_{0.7}Mg_{0.3}Ni_{3.5-x}(Al_{0.5}Mo_{0.5})_x$ with x = 0–0.8 [85]) decreased the desorption equilibrium pressure.

## 6. Solid Solutions

Metallurgically speaking, the term "solid solution alloy" designates a primary element (solvent) into which one or more minor elements (solutes) are dissolved. Unlike the intermetallic compound, the solute does not need to be present at an integer or near-integer stoichiometric ratio and is present in a random (disordered) substitutional or interstitial distribution within the basic crystal structure. Several solid solution alloys form reversible hydrides, in particular those based on Pd, Ti, Zr, Nb and V solvents [86].

Despite excellent properties such as fast absorption/desorption kinetics and large hydrogen gravimetric density of maximum 3.8 wt% at moderate temperatures, V-based alloys suffer major drawbacks preventing their rapid and widespread applications. These limitations are (i) the relatively difficult first activation, and (ii) the high thermal stability of its hydride phases yielding poor cyclic performance (reversible capacity down to ~2 wt% $H_2$ at room temperature) [87].

Upon hydrogenation, V forms a solid solution α followed by β phase ($V_2H$ with body-centered tetragonal structure) and then the γ phase ($VH_2$ with $CaF_2$ crystal structure), whose respective thermal stability drastically differs. Indeed, the β phase is so stable that its hydrogen desorption reaction never occurs under moderate conditions, its desorption pressure usually ranging $10^{-5}$–0.1 atm. On the other hand, the γ phase is not as stable as its β counterpart and its hydrogen absorption/desorption reaction occurs at moderate temperatures and pressures (over 1 atm at room temperature). Therefore, due to the stability of the β phase, only about half of the amount of hydrogen absorbed in vanadium metal can be used in the hydrogen absorption and desorption processes under practical conditions [87].

Thermodynamic destabilization of the β phase of pristine V stands out as the main solution to tackle the issues mentioned above. Hence, similarly to any other $A_xB_y$ alloy category, the use of alloying elements of diverse nature and simultaneous addition (binary, ternary and quaternary systems for instance) can destabilize the hydride phases, by altering the ionicity, electronic density of states and lattice parameters [88].

Binary V-based systems cover a broad range of elements, with Ti being the most studied one in the light of its high solubility in V [89], the improved hydrogenation rates and increased terminal solid solubility (TSS) of hydrogen [88]. Although Ti is widely utilized, other elements such as Si, Al and Fe are also considered, but turn out to decrease the hydrogenation rates [90][91], while Mo addition increases hydrogenation-dehydrogenation pressure and decreases the hydrogen storage capacity for instance [92].

To push further the enhancement brought by binary alloys, ternary systems have been developed, notably V–Ti–Cr which remains the most documented ternary alloy due to its excellent improvement of the cyclic stability (as compared to its former binary V–Ti counterpart) while maintaining high effective capacity at room temperature [93][94][95]. Storage capacity can be controlled and increased by tuning the compositional ratio of those three elements, for instance in a mixture of 60 at% V, 15 at% Ti and 25 at% Cr which reaches as high as 2.62 wt% [96] V–Ti–Cr alloys however show a steep slope of

hydrogen absorption–desorption plateaus, requiring homogenization by heat treatment [97][98] and melt-quenching treatment [99][100]. Besides, the formation of an enriched Ti phase during heat treatment and the oxidation of Ti during melt-quenching both reduce the amount of stored hydrogen and complicate the activation process [101].

In spite of the attractive storage capacity of V–Ti–Cr alloys, they remain expensive since the price of pure V is very high. Fe can thus be used as a replacement of V in ternary systems, and excellent storage capacity of 3.9 wt% with a reversible capacity of 2.4 wt% are reported for $Ti_{43.5}V_{49}Fe_{7.5}$ (at 253 K) [102]. Fe also shows a great potential for tailoring plateau pressures, for instance in $(V_{0.9}Ti_{0.1})_{1-x}Fe$ alloys (with x = 0–0.075) [103]. The reduction of costs by Fe addition has also been attempted for quaternary alloys, notably by Luo et al. [104] who synthesized $V_{48}Fe_{12}Ti_{15}Cr_{25}$. The maximum hydrogen storage capacity of this alloy reached 1.98 wt% at 315 K, which is lower than that of other V–Ti–Cr series alloys, due to smaller lattice constant and cell volume.

The lattice constant of the alloys is closely related to the amount of hydrogen absorbed/desorbed [105][106]: $V_{48}Fe_{12}Ti_{15}Cr_{25}$ has smaller interstitial sites, which could lead to a lower hydrogen storage capacity, higher plateau pressure, and smaller hysteresis. Similar to Fe addition, the use of Ce is shown by Liu et al. [107] to improve the flatness of plateau of the $Ti_{32}Cr_{46}V_{22}$ BCC alloy, as a result of the microstructural homogenization during heat-treatment (Ce also increases the hydrogen capacity by lowering the oxygen concentration). The heat-treated $Ti_{32}Cr_{46}V_{22}Ce_{0.4}$ alloy can release 2.00 and 2.52 wt% $H_2$ at 343 and 298 K, respectively, under 1 atm.

In general, quaternary alloys compile the advantages of the already optimized properties of ternary V–Ti–Cr alloys, and display an improved cyclic stability without noticeable change of the storage capacity after the addition of various atoms such as Fe [108], Nb [109] or even C [110]. However, even more complex systems exist, as shown by Yang et al. [111], who conducted partial substitution studies on V–Ti–Cr–Fe alloys using Co and Zr for improving the storage and cyclic properties. They found out that the hydrogen absorption-desorption capacities of the $(VFe)_{60}(TiCrCo)_{40-x}Zr_x$ alloys decrease with increasing Zr content. The maximum desorption capacity reaches 2.10 wt% when x = 0, against 1.88 wt% when x = 2. This could be ascribed to the decrease of the volume fraction of the BCC phase while the other phases increase with the Zr content. At the same time, the rate of cyclic degradation decreases with higher Zr content, from 10.9% after 10 cycles (for x = 0) down to 4.5% (when x = 2). Moreover, as the Zr content increases, the hydriding incubation period shortens from 120 s for x = 0 down to 4 s for x = 2. Additionally, more than 90% of the maximum hydrogen absorption capacity is achieved in 400 s when x = 0, while only about 150 s when x = 2. Figure 8 shows the desorption behaviour of some representative solid solution alloys described in this section.

## References

1. 1. Schlapbach, L.; Züttel, A. Hydrogen-Storage Materials for Mobile Applications. In Materials for Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group; World Scientific: Singpore, 2011; pp. 265–270.

2. Principi, G.; Agresti, F.; Maddalena, A.; Russo, S.L. The problem of solid state hydrogen storage. Energy 2009, 34, 2087–2091, doi:10.1016/j.energy.2008.08.027.

3. US Department of Energy. DOE Technical Targets for Onboard Hydrogen Storage for Light-Duty Vehicles; Office of Energy Efficiency and Renewable Energy: Washington, DC, USA, 2017.

4. Borzone, E.; Baruj, A.; Blanco, M.; Meyer, G. Dynamic measurements of hydrogen reaction with LaNi5−xSnx alloys. Int. J. Hydrogen Energy 2013, 38, 7335–7343, doi:10.1016/j.ijhydene.2013.04.035.

5. Modibane, K.; Lototskyy, M.V.; Davids, M.; Williams, M.; Hato, M.; Molapo, K. Influence of co-milling with palladium black on hydrogen sorption performance and poisoning tolerance of surface modified AB5-type hydrogen storage alloy. J. Alloy. Compd. 2018, 750, 523–529, doi:10.1016/j.jallcom.2018.04.003.

6. Pan, H.; Liu, Y.; Gao, M.; Zhu, Y.; Lei, Y. The structural and electrochemical properties of La0.7Mg0.3 (Ni0.85Co0.15)x (x = 3.0–5.0) hydrogen storage alloys. Int. J. Hydrogen Energy 2003, 28, 1219–1228.

7. Sharma, V.K.; Kumar, E.A. Effect of measurement parameters on thermodynamic properties of La-based metal hydrides. Int. J. Hydrogen Energy 2014, 39, 5888–5898, doi:10.1016/j.ijhydene.2014.01.174.

8. Prigent, J.; Joubert, J.-M.; Gupta, M. Modification of the hydrogenation properties of LaNi5 upon Ni substitution by Rh, Ir, Pt or Au. J. Alloy. Compd. 2012, 511, 95–100, doi:10.1016/j.jallcom.2011.08.094.

9. Georgiadis, M.C.; Kikkinides, E.; Makridis, S.S.; Kouramas, K.; Pistikopoulos, E.N. Design and optimization of advanced materials and processes for efficient hydrogen storage. Comput. Chem. Eng. 2009, 33, 1077–1090, doi:10.1016/j.compchemeng.2008.09.009.

10. Liu, J.J.; Li, K.; Cheng, H.H.; Yan, K.; Wang, Y.; Liu, Y.; Jin, H.M.; Zheng, Z. New insights into the hydrogen storage performance degradation and Al functioning mechanism of LaNi5−xAlx alloys. Int. J. Hydrogen Energy 2017, 42, 24904–24914.

11. Zhu, Y.; Yang, C.; Zhu, J.; Li, L. Structural and electrochemical hydrogen storage properties of Mg2Ni-based alloys. J. Alloy. Compd. 2011, 509, 5309–5314, doi:10.1016/j.jallcom.2011.02.017.

12. Pęska, M.; Dworecka-Wójcik, J.; Płociński, T.; Polański, M. The Influence of Cerium on the Hydrogen Storage Properties of La1−xCexNi5 Alloys. Energies 2020, 13, 1437, doi:10.3390/en13061437.

13. Chen, J.; Dou, S.; Liu, H.K. Effect of partial substitution of La with Ce, Pr and Nd on the properties of LaNi5-based alloy electrodes. J. Power Sources 1996, 63, 267–270, doi:10.1016/s0378-7753(96)02461-5.

14. Balasubramaniam, R.; Mungole, M.; Rai, K. Hydriding properties of MmNi5 system with aluminium, manganese and tin substitutions. J. Alloy. Compd. 1993, 196, 63–70, doi:10.1016/0925-8388(93)90571-4.

15. Mungole, M. Hysteresis in MmNi5 systems with aluminium, manganese and tin substitutions. Int. J. Hydrogen Energy 1995, 20, 151–157, doi:10.1016/0360-3199(94)e0014-p.

16. Molinas, B.; Pontarollo, A.; Scapin, M.; Peretti, H.; Melnichuk, M.; Corso, H.; Aurora, A.; Gattia, D.M.; Montone, A. The optimization of MmNi5−xAlx hydrogen storage alloy for sea or lagoon navigation and transportation. Int. J. Hydrogen Energy 2016, 41, 14484–14490.

17. Iosub, V.; Latroche, M.; Joubert, J.-M.; Percheron-Guégan, A. Optimisation of MmNi5−xSnx (Mm = La, Ce, Nd and Pr, 0.27< x< 0.5) compositions as hydrogen storage materials. Int. J. Hydrogen Energy 2006, 31, 101–108.

18. Zhou, W.; Tang, Z.; Zhu, D.; Ma, Z.; Wu, C.; Huang, L.; Chen, Y. Low-temperature and instantaneous high-rate output performance of AB5-type hydrogen storage alloy with duplex surface hot-alkali treatment. J. Alloy. Compd. 2017, 692, 364–374, doi:10.1016/j.jallcom.2016.08.292.

19. Srivastava, S.; Upadhyaya, R. Investigations on synthesis, characterization and hydrogenation behavior of hydrogen storage alloys, Mm1−xCaxNi5−y−zAlyFez (x = 0, 0.05, 0.1, 0.2, 0.3; y = 0, 0.1; z = 0, 0.1) Mm1−xCaxNi5−y−zAlyFez (x = 0,0.05,0.1,0.2,0.3; y = 0,0.1; z = 0, 0.1). Int. J. Hydrogen Energy 2007, 32, 4195–4201, doi:10.1016/j.ijhydene.2007.06.011.

20. Srivastava, S.; Upadhyaya, R. Investigations of AB5-type hydrogen storage materials with enhanced hydrogen storage capacity. Int. J. Hydrogen Energy 2011, 36, 7114–7121, doi:10.1016/j.ijhydene.2011.02.111.

21. Sandrock, G. A New Family of Hydrogen Storage Alloys Based on the System Nickel-Mischmetal-Calcium. In Proceedings of the 12th Intersociety Energy Conversion Engineering Conference, Washington, DC, USA, 28 August–2 September 1977, pp. 951–958.

22. Shinar, J.; Shaltiel, D.; Davidov, D.; Grayevsky, A. Hydrogen sorption properties of the La1−xCaxNi5 and La (Ni1−xCux)5 systems. J. Comm. Metals 1978, 60, 209–219.

23. Wang, X.; Chen, C.; Wang, C.; Wang, Q. Hydrogen storage properties of Ml1−xCaxNi5 pseudobinary intermetallic compounds. J. Alloys Compd. 1996, 232, 192–196.

24. Kumar, E.A.; Sharma, V. Simulation of Pressure Concentration Isotherms of MmNi5−xAlx Hydrides. In Proceedings of the 13th International Conference on Fuel Cell & Hydrogen Technologies, Kuala Lumpur, Malaysia, 22–23 November 2011.

25. Sarma, V. On the mechanically pulverized MmNi4.6Fe0.4 as a viable hydrogen storage material. Int. J. Hydrogen Energy 2001, 26, 231–236, doi:10.1016/s0360-3199(00)00060-4.

26. Apostolov, A.; Stanev, N.; Tcholakov, P. Hydrogen desorption characteristics of MmNi5−xFex compounds. J. Less Common Met. 1985, 110, 127–129, doi:10.1016/0022-5088(85)90313-3.

27. Bououdina, M.; Grant, D.M.; Walker, G. Review on hydrogen absorbing materials—structure, microstructure, and thermodynamic properties. Int. J. Hydrogen Energy 2006, 31, 177–182, doi:10.1016/j.ijhydene.2005.04.049.

28. Kim, M.-H.; Debnath, M.R.; Wang, Y.-I.; Suh, J.-Y.; Fleury, E.; Kim, D. Effect of Co on the degradation of the hydrogen permeability of Ni–Nb–Zr amorphous membranes. Met. Mater. Int. 2014, 20, 215–219, doi:10.1007/s12540-014-2004-y.

29. Zhao, Y.; Choi, I.-C.; Seok, M.-Y.; Kim, M.-H.; Kim, D.-H.; Ramamurty, U.; Suh, J.-Y.; Jang, J.-I. Effect of hydrogen on the yielding behavior and shear transformation zone volume in metallic glass ribbons. Acta Mater. 2014, 78, 213–221, doi:10.1016/j.actamat.2014.06.046.

30. Zhao, Y.; Choi, I.-C.; Seok, M.-Y.; Ramamurty, U.; Suh, J.-Y.; Jang, J.-I. Hydrogen-induced hardening and softening of Ni–Nb–Zr amorphous alloys: Dependence on the Zr content. Scr. Mater. 2014, 93, 56–59, doi:10.1016/j.scriptamat.2014.08.029.

31. Fadonougbo, J.O.; Suh, J.-Y.; Han, S.; Shim, C.-H.; Kim, G.-H.; Kim, M.-H.; Fleury, E.; Cho, Y.W. Hydrogen-induced decomposition of Cu–Zr binary amorphous metallic alloys. J. Alloy. Compd. 2016, 660, 456–460, doi:10.1016/j.jallcom.2015.11.113.

32. Fadonougbo, J.O.; Suh, J.-Y.; Shim, C.-H.; Kim, G.-H.; Fleury, E.; Cho, Y.W. Nanometer-scale phase separation and formation of delta ZrH2 in Cu–Zr binary amorphous alloys. J. Alloy. Compd. 2017, 721, 646–652, doi:10.1016/j.jallcom.2017.06.012.

33. Park, J.-G.; Jang, H.-Y.; Han, S.-C.; Lee, P.S.; Lee, J.-Y. The thermodynamic properties of Ti–Zr–Cr–Mn laves phase alloys. J. Alloys Compd 2001, 325, 293–298.

34. Liu, B.-H.; Kim, N.-M.; Lee, K.-Y.; Lee, J.-Y. Hydrogen storage properties of TiMn2-based alloys. J. Alloy. Compd. 1996, 240, 214–218, doi:10.1016/0925-8388(96)02245-1.

35. Kojima, Y.; Kawai, Y.; Towata, S.-I.; Matsunaga, T.; Shinozawa, T.; Kimbara, M. Development of metal hydride with high dissociation pressure. J. Alloy. Compd. 2006, 419, 256–261, doi:10.1016/j.jallcom.2005.08.078.

36. Kandavel, M.; Bhat, V.; Rougier, A.; Aymard, L.; Nazri, G.-A.; Tarascon, J.-M. Improvement of hydrogen storage properties of the AB2 Laves phase alloys for automotive application. Int. J. Hydrogen Energy 2008, 33, 3754–3761, doi:10.1016/j.ijhydene.2008.04.042.

37. Park, J.-G.; Jang, H.-Y.; Han, S.-C.; Lee, P.S.; Lee, J.-Y. The thermodynamic properties of Ti–Zr–Cr–Mn laves phase alloys. J. Alloys Compd 2001, 325, 293–298.

38. Morii, K.; Shimizu, T. Hydriding characteristics in (Ti,Zr)(Ni,Mn,X)2 alloys. J. Alloy. Compd. 1995, 231, 524–527, doi:10.1016/0925-8388(95)01860-3.

39. Manickam, K.; Grant, D.M.; Sardari, P.T. Optimization of AB2 type alloy composition with superior hydrogen storage properties for stationary applications. Int. J. Hydrogen Energy 2015, 40, 16288–16296, doi:10.1016/j.ijhydene.2015.09.157.

40. Li, J.; Jiang, X.; Li, G.; Li, X. Development of Ti1.02Cr2−x−yFexMny (0.6 ≤ x ≤ 0.75, y = 0.25, 0.3) alloys for high hydrogen pressure metal hydride system. Int. J. Hydrogen Energy 2019, 44, 15087–15099.

41. Corgnale, C.; Sulic, M. Techno-Economic Analysis of High-Pressure Metal Hydride Compression Systems. Metals 2018, 8, 469, doi:10.3390/met8060469.

42. Pickering, L.; Lototskyy, M.V.; Davids, M.W.; Sita, C.; Linkov, V. Induction melted AB2-type metal hydrides for hydrogen storage and compression applications. Mater. Today: Proc. 2018, 5, 10470–10478, doi:10.1016/j.matpr.2017.12.378.

43. Ulmer, U.; Dieterich, M.; Pohl, A.; Dittmeyer, R.; Linder, M.P.; Fichtner, M. Study of the structural, thermodynamic and cyclic effects of vanadium and titanium substitution in laves-phase AB2 hydrogen storage alloys. Int. J. Hydrogen Energy 2017, 42, 20103–20110, doi:10.1016/j.ijhydene.2017.06.137.

44. Yao, Z.; Liu, L.; Xiao, X.; Wang, C.; Jiang, L.; Chen, L. Effect of rare earth doping on the hydrogen storage performance of Ti1.02Cr1.1Mn0.3Fe0.6 alloy for hybrid hydrogen storage application. J. Alloy. Compd. 2018, 731, 524–530, doi:10.1016/j.jallcom.2017.10.075.

45. Puszkiel, J.; Bellosta von Colbe, J.M.; Jepsen, J.; Mitrokhin, S.V.; Movlaev, E.; Verbetsky, V.; Klassen, T. Designing an AB2-Type Alloy (TiZr-CrMnMo) for the Hybrid Hydrogen Storage Concept. Energies 2020, 13, 2751.

46. Wu, T.; Xue, X.; Zhang, T.; Hu, R.; Kou, H.; Li, J. Role of Ni addition on hydrogen storage characteristics of ZrV2 Laves phase compounds. Int. J. Hydrogen Energy 2016, 41, 10391–10404, doi:10.1016/j.ijhydene.2014.10.023.

47. Qin, C.; Zhou, C.; Ouyang, L.; Liu, J.; Zhu, M.; Sun, T.; Wang, H. High-pressure hydrogen storage performances of ZrFe2 based alloys with Mn, Ti, and V addition. Int. J. Hydrogen Energy 2020, 45, 9836–9844, doi:10.1016/j.ijhydene.2019.11.242.

48. Zhou, C.; Wang, H.; Ouyang, L.; Liu, J.; Zhu, M. Achieving high equilibrium pressure and low hysteresis of Zr–Fe based hydrogen storage alloy by Cr/V substitution. J. Alloy. Compd. 2019, 806, 1436–1444, doi:10.1016/j.jallcom.2019.07.170.

49. Qin, C.; Zhou, C.; Ouyang, L.; Liu, J.; Zhu, M.; Sun, T.; Wang, H. High-pressure hydrogen storage performances of ZrFe2 based alloys with Mn, Ti, and V addition. Int. J. Hydrogen Energy 2020, 45, 9836–9844, doi:10.1016/j.ijhydene.2019.11.242.

50. Zhou, C.; Wang, H.; Ouyang, L.; Liu, J.; Zhu, M. Achieving high equilibrium pressure and low hysteresis of Zr–Fe based hydrogen storage alloy by Cr/V substitution. J. Alloy. Compd. 2019, 806, 1436–1444, doi:10.1016/j.jallcom.2019.07.170.

51. Blasius, A.; Gonster, U. Mössbauer surface studies on Tife hydrogen storage material. Appl. Phys. A 1980, 22, 331–332, doi:10.1007/bf00899887.

52. Reilly, J.J.; Wiswall, R.H. Formation and properties of iron titanium hydride. Inorg. Chem. 1974, 13, 218–222, doi:10.1021/ic50131a042.

53. Sandrock, G.D.; Reilly, J.J.; Johnson, J.R. Metallurgical Considerations in the Production and use of FeTi Alloys for Hydrogen Storage. In Proceedings of the Intersociety Energy Conversion Engineering Conference, State Line, NV, USA, 12 September 1976.

54. Edalati, K.; Matsuda, J.; Iwaoka, H.; Toh, S.; Akiba, E.; Horita, Z. High-pressure torsion of TiFe intermetallics for activation of hydrogen storage at room temperature with heterogeneous nanostructure. Int. J. Hydrogen Energy 2013, 38, 4622–4627, doi:10.1016/j.ijhydene.2013.01.185.

55. Davids, M.W.; Lototskyy, M.V.; Nechaev, A.; Naidoo, Q.; Williams, M.; Klochko, Y. Surface modification of TiFe hydrogen storage alloy by metal-organic chemical vapour deposition of palladium. Int. J. Hydrogen Energy 2011, 36, 9743–9750, doi:10.1016/j.ijhydene.2011.05.036.

56. Qu, H.; Du, J.; Pu, C.; Niu, Y.; Huang, T.; Li, Z.; Lou, Y.; Wu, Z. Effects of Co introduction on hydrogen storage properties of Ti–Fe–Mn alloys. Int. J. Hydrogen Energy 2015, 40, 2729–2735.

57. Yamashita, I.; Tanaka,H.; Takeshita, H.; Kuriyama,N.; Sakai, T.; Uehara, I. Hydrogenation characteristics of TiFe1−xPdx (0.05 ≤ x ≤ 0.30) alloys. J. Alloys Compd. 1997, 253, 238–240.

58. Jang, T.; Han, J.; Jai-Young, L. Effect of substitution of titanium by zirconium in TiFe on hydrogenation properties. J. Less Common Met. 1986, 119, 237–246, doi:10.1016/0022-5088(86)90684-3.

59. Bronca, V.; Bergman, P.; Ghaemmaghami, V.; Khatamian, D.; Manchester, F. Hydrogen absorption characteristics of an FeTi + misch metal alloy. J. Less Common Met. 1985, 108, 313–325, doi:10.1016/0022-5088(85)90226-7.

60. Guéguen, A.; Latroche, M. Influence of the addition of vanadium on the hydrogenation properties of the compounds TiFe0.9Vx and TiFe0.8Mn0.1Vx (x = 0, 0.05 and 0.1). J. Alloy. Compd. 2011, 509, 5562–5566, doi:10.1016/j.jallcom.2011.02.036.

61. Lee, S.M.; Perng, T.P. Microstructural Correlations with the Hydrogenation Kinetics of FeTi1+ε Alloys, J. Alloys Compd. 1991, 177, 107–118.

62. Emami, H.; Edalati, K.; Matsuda, J.; Akiba, E.; Horita, Z. Hydrogen storage performance of TiFe after processing by ball milling. Acta Mater. 2015, 88, 190–195, doi:10.1016/j.actamat.2014.12.052.

63. Chiang, C.-H.; Chin, Z.-H.; Perng, T.-P. Hydrogenation of TiFe by high-energy ball milling. J. Alloy. Compd. 2000, 307, 259–265, doi:10.1016/s0925-8388(00)00827-6.

64. Davids, M.W.; Lototskyy, M.V.; Nechaev, A.; Naidoo, Q.; Williams, M.; Klochko, Y. Surface modification of TiFe hydrogen storage alloy by metal-organic chemical vapour deposition of palladium. Int. J. Hydrogen Energy 2011, 36, 9743–9750, doi:10.1016/j.ijhydene.2011.05.036.

65. Edalati, K.; Matsuda, J.; Yanagida, A.; Akiba, E.; Horita, Z. Activation of TiFe for hydrogen storage by plastic deformation using groove rolling and high-pressure torsion: Similarities and differences. Int. J. Hydrogen Energy 2014, 39, 15589–15594, doi:10.1016/j.ijhydene.2014.07.124.

66. Yang, T.; Wang, P.; Xia, C.Q.; Liu, N.; Liang, C.Y.; Yin, F.X.; Li, Q. Effect of chromium, manganese and yttrium on microstructure and hydrogen storage properties of TiFe-based alloy. Int. J. Hydrogen Energy 2020, 45, 12071–12081.

67. Ha, T.; Lee, S.-I.; Hong, J.; Lee, Y.-S.; Kim, D.-I.; Suh, J.-Y.; Cho, Y.W.; Hwang, B.; Lee, J.; Shim, J.-H. Hydrogen storage behavior and microstructural feature of a TiFe–ZrCr2 alloy. J. Alloy. Compd. 2021, 853, 157099, doi:10.1016/j.jallcom.2020.157099.

68. Jung, J.Y.; Lee, Y.-S.; Suh, J.-Y.; Huh, J.-Y.; Cho, Y.W. Tailoring the equilibrium hydrogen pressure of TiFe via vanadium substitution. J. Alloy. Compd. 2021, 854, 157263, doi:10.1016/j.jallcom.2020.157263.

69. Ouyang, L.; Huang, J.; Wang, H.; Liu, J.; Zhu, M. Progress of hydrogen storage alloys for Ni–MH rechargeable power batteries in electric vehicles: A review. Mater. Chem. Phys. 2017, 200, 164–178, doi:10.1016/j.matchemphys.2017.07.002.

70. Liu, Y.; Pan, H.; Yue, Y.; Wu, X.; Chen, N.; Lei, Y. Cycling durability and degradation behavior of La–Mg–Ni–Co-type metal hydride electrodes. J. Alloy. Compd. 2005, 395, 291–299.

71. Liao, B.; Lei, Y.; Chen, L.; Lü, G.; Pan, H.; Wang, Q. The effect of Al substitution for Ni on the structure and electrochemical properties of AB3-type La2Mg(Ni1−xAlx)9 (x = 0–0.05) alloys. J. Alloy. Compd. 2005, 404, 665–668, doi:10.1016/j.jallcom.2004.10.088.

72. Liu, W.; Webb, C.; Gray, E. Review of hydrogen storage in AB3 alloys targeting stationary fuel cell applications. Int. J. Hydrogen Energy 2016, 41, 3485–3507, doi:10.1016/j.ijhydene.2015.12.054.

73. Takeshita, T.; Wallace, W.E.; Craig, R.S. Solubility of hydrogen in rare earth-tricobalt compounds. Inorg. Chem. 1974, 13, 2283–2284, doi:10.1021/ic50139a051.

74. Oesterreicher, H.; Clinton, J.; Bittner, H. Hydrides of La–Ni Compounds. Mater. Res. Bull. 1976, 11, 1241–1247.

75. Kadir, K.; Sakai, T.; Uehara, I. Synthesis and structure determination of a new series of hydrogen storage alloys; RMg2Ni9 (R=La, Ce, Pr, Nd, Sm and Gd) built from MgNi2 Laves-type layers alternating with AB5 layers. J. Alloy. Compd. 1997, 257, 115–121, doi:10.1016/s0925-8388(96)03132-5.

76. Kadir, K.; Sakai, T.; Uehara, I. Structural investigation and hydrogen capacity of YMg2Ni9 and (Y0.5Ca0.5)(MgCa)Ni9: new phases in the AB2C9 system isostructural with LaMg2Ni9. J. Alloy. Compd. 1999, 287, 264–270.

77. Kadir, K.; Sakai, T.; Uehara, I. Structural investigation and hydrogen storage capacity of LaMg2Ni9 and (La0.65Ca0.35)(Mg1.32Ca0.68)Ni9 of the AB2C9 type structure. J. Alloy. Compd. 2000, 302, 112–117, doi:10.1016/s0925-8388(00)00581-8.

78. Chen, J.; Kuriyama, N.; Takeshita, H.; Tanaka, H.; Sakai, T.; Haruta, M. Hydrogen Storage Alloys with PuNi3-Type Structure as Metal Hydride Electrodes. Electrochem. Solid State Lett. 2000, 3, 249–252.

79. Kadir, K.; Sakai, T.; Uehara, I. Structural investigation and hydrogen storage capacity of LaMg2Ni9 and (La0.65Ca0.35)(Mg1.32Ca0.68)Ni9 of the AB2C9 type structure. J. Alloy. Compd. 2000, 302, 112–117, doi:10.1016/s0925-8388(00)00581-8.

80. Lim, K.L.; Liu, Y.; Zhang, Q.-A.; Chan, S.L.I. Effects of partial substitutions of cerium and aluminum on the hydrogenation properties of La (0.65−x) CexCa1. 03Mg1. 32Ni (9−y) Aly alloy. Int. J. Hydrogen Energy 2014, 39, 10537–10545.

81. Xin, G.; Wang, S.; Yuan, H.; Yang, K.; Jiang, L.; Liu, X. Promising hydrogen storage properties of cost-competitive La(Y)–Mg–Ca–Ni AB3-type alloys for stationary applications. RSC Adv. 2016, 6, 21742–21748, doi:10.1039/C6RA01585A.

82. Zang, J.; Zhang, Q.; Sun, D. Hydrogen storage performances of RCaMgNi9 (R = Nd, Gd and Er) compounds. J. Alloy. Compd. 2019, 794, 45–52, doi:10.1016/j.jallcom.2019.04.236.

83. Liu, Y.; Pan, H.; Gao, M.; Li, R.; Lei, Y. Effect of Co content on the structural and electrochemical properties of the La0.7Mg0.3Ni3.4−xMn0.1Cox hydride alloys: II. Electrochemical properties. J. Alloy. Compd. 2004, 376, 304–313.

84. Liao, B.; Lei, Y.; Chen, L.; Lü, G.; Pan, H.; Wang, Q. Effect of Co substitution for Ni on the structural and electrochemical properties of La2Mg(Ni1−xCox)9 (x = 0.1–0.5) hydrogen storage electrode alloys. Electrochim. Acta 2004, 50, 1057–1063, doi:10.1016/j.electacta.2004.08.004.

85. Zhang, X.; Sun, D.; Yin, W.; Chai, Y.; Zhao, M. Crystallographic and electrochemical characteristics of La0.7Mg0.3Ni3.5 − x (Al0.5Mo0.5)x (x = 0–0.8) hydrogen storage alloys. J. Power Sour. 2006, 154, 290–297.

86. Sandrock, G. A panoramic overview of hydrogen storage alloys from a gas reaction point of view. J. Alloy. Compd. 1999, 293, 877–888, doi:10.1016/s0925-8388(99)00384-9.

87. Yukawa, H.; Takagi, M.; Teshima, A.; Morinaga, M. Alloying effects on the stability of vanadium hydrides. J. Alloy. Compd. 2002, 330, 105–109, doi:10.1016/s0925-8388(01)01526-2.

88. Kumar, S.; Jain, A.; Ichikawa, T.; Kojima, Y.; Dey, G. Development of vanadium based hydrogen storage material: A review. Renew. Sustain. Energy Rev. 2017, 72, 791–800, doi:10.1016/j.rser.2017.01.063.

89. Seo, C.-Y.; Kim, J.-H.; Lee, P.S.; Lee, J.-Y. Hydrogen storage properties of vanadium-based b.c.c. solid solution metal hydrides. J. Alloy. Compd. 2003, 348, 252–257, doi:10.1016/s0925-8388(02)00831-9.

90. Kumar, S.; Taxak, M.; Krishnamurthy, N. Hydrogen absorption kinetics of V–Al alloy. J. Therm. Anal. Calorim. 2013, 112, 5–10.

91. Kumar, S.; Taxak, M.; Krishnamurthy, N. Synthesis and hydrogen absorption kinetics of V4Cr4Ti alloy. J. Therm. Anal. Calorim. 2012, 112, 51–57, doi:10.1007/s10973-012-2643-5.

92. Verbetsky, V.N.; Zotov, T.A.; Movlaev, E.A. Absorption of hydrogen by V–Mo and V–Mo–Ti alloys. Inorg. Mater. Appl. Res. 2014, 5, 70–74, doi:10.1134/s2075113314010134.

93. Tamura, T.; Kazumi, T.; Kamegawa, A.; Takamura, H.; Okada, M. Protium absorption properties and protide formations of Ti–Cr–V alloys, J. Alloy. Compd. 2003, 356, 505–509.

94. Okada, M.; Kuriiwa, T.; Tamura, T.; Takamura, H.; Kamegawa, A. Ti–V–Cr bcc alloys with high protium content. J. Alloy. Compd. 2002, 330, 511–516.

95. Kagawa, A.; Ono, E.; Kusakabe, T.; Sakamoto, Y. Absorption of Hydrogen by Vanadium-Rich V–Ti-Based Alloys. J. Less Common Metals 1991, 172, 64–70.

96. Tsukahara, M. Hydrogenation Properties of Vanadium-Based Alloys with Large Hydrogen Storage Capacity. Mater. Trans. 2011, 52, 68–72, doi:10.2320/matertrans.m2010216.

97. Tamura, T.; Tominaga, Y.; Matsumoto, K.; Fuda, T.; Kuriiwa, T.; Kamegawa, A.; Takamura, H.; Okada, M.; Protium absorption properties of Ti–V–Cr–Mn alloys with a bcc structure. J. Alloy. Compd. 2002, 330, 522–525.

98. Shudo, Y.; Ebisawa, T.; Itoh, H. Characterization of Ti–Zr–Mn–V-based Laves phase alloys for MH refrigeration system. J. Alloy. Compd. 2003, 356, 497–500.

99. Yu, X.; Wu, Z.; Xia, B.; Xu, N. Hydrogen storage performance of quenched Ti–V-based alloy. J. Alloy. Compd. 2004, 373, 134–136, doi:10.1016/j.jallcom.2003.10.030.

100. Yu, X.; Wu, Z.; Xu, N. Effects of melt-quenching rates on the hydrogen storage properties of Ti-based BCC phase alloy. Phys. B Condens. Matter 2004, 344, 456–461, doi:10.1016/j.physb.2003.11.002.

101. Yu, X.; Wu, Z.; Xia, B.; Xu, N. Improvement of activation performance of the quenched Ti–V-based BCC phase alloys. J. Alloy. Compd. 2005, 386, 258–260, doi:10.1016/j.jallcom.2004.05.014.

102. Nomura, K.; Akiba, E. H2 Absorbing-desorbing characterization of the TiVFe alloy system. J. Alloy. Compd. 1995, 231, 513–517, doi:10.1016/0925-8388(95)01862-x.

103. Lynch, J.F.; Maeland, A.J.; Libowitz, G.G. Lattice Parameter Variation and Thermodynamics of Dihydride Formation in the Vanadium-Rich V–Ti–Fe/H2 System. Zeitschrift für Physikalische Chemie 1985, 145, 51–59, doi:10.1524/zpch.1985.145.1_2.051.

104. Luo, L.; Li, Y.; Zhai, T.; Hu, F.; Zhao, Z.; Bian, X.; Wu, W. Microstructure and hydrogen storage properties of V48Fe12Ti15-xCr25Alx (x = 0, 1) alloys. Int. J. Hydrogen Energy 2019, 44, 25188–25198.

105. Akiba, E.; Iba, H. Hydrogen absorption by Laves phase related BCC solid solution. Intermetallics 1998, 6, 461–470, doi:10.1016/s0966-9795(97)00088-5.

106. Yan, Y.; Chen, Y.; Liang, H.; Wu, C.; Tao, M.; Mingjing, T. Effect of Al on hydrogen storage properties of V30Ti35Cr25Fe10 alloy. J. Alloy. Compd. 2006, 426, 253–255, doi:10.1016/j.jallcom.2005.12.122.

107. Liu, X.; Jiang, L.; Li, Z.; Huang, Z.; Wang, S. Improve plateau property of Ti32Cr46V22 BCC alloy with heat treatment and Ce additive. J. Alloy. Compd. 2009, 471, L36–L38, doi:10.1016/j.jallcom.2008.04.004.

108. Aoki, M.; Noritake, T.; Ito, A.; Ishikiriyama, M.; Towata, S.-I. Improvement of cyclic durability of Ti–Cr–V alloy by Fe substitution. Int. J. Hydrogen Energy 2011, 36, 12329–12332.

109. Towata, S.-I.; Noritake, T.; Itoh, A.; Aoki, M.; Miwa, K. Effect of partial niobium and iron substitution on short-term cycle durability of hydrogen storage Ti–Cr–V alloys. Int. J. Hydrogen Energy 2013, 38, 3024–3029, doi:10.1016/j.ijhydene.2012.12.100.

110. Shen, C.-C.; Li, H.-C. Cyclic hydrogenation stability of γ-hydrides for Ti25V35Cr40 alloys doped with carbon. J. Alloy. Compd. 2015, 648, 534–539, doi:10.1016/j.jallcom.2015.07.021.

111. Yang, S.; Yang, F.; Wu, C.; Chen, Y.; Mao, Y.; Luo, L. Hydrogen storage and cyclic properties of (VFe)60(TiCrCo)40-xZrx (0≤ x ≤ 2) alloys. J. Alloy. Compd. 2016, 663, 460–465.