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NEW METAL HYDRIDES FOR HYDROGEN STORAGE IN PEM FUEL CELL SYSTEMS

Schlussbericht

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Inhaltsverzeichnis

Zusammenfassung

Metallhydride speichern Wasserstoff energieeffizient, kompakt und sicher. Wir haben die folgenden komplexen *d*- and *p*- Metallhydride für mögliche Anwendungen, insbesondere in PEM Brennstoffzellensystemen, synthetisiert. Die Magnesium-Eisenverbindung Mg_2FeH_6 wurde kostengünstig in der Kugelmühle mit einer Ausbeute von 91% hergestellt, was im Vergleich zur früheren Ausbeute von 80% einen neuen Rekord darstellt. Um die thermische Stabilität zu verringern und die Desorptionskinetik zu erhöhen wurde die Verbindung mit einigen At.% $TiCl_3$ und Nb_2O_5 "gedopt". Die Ergebnisse bestätigen den positive Einfluss der Dopierung auf die Kinetik, besonders am Beginn der Desorption, zeigen aber auch, dass die Thermodynamik nahezu unbeeinflusst bleibt. Hingegen steigert Langzeitmahlen in der Kugelmühle den Wasserstoffgleichgewichtsdruck um ~0.1 bar, d.h. es destabilisiert die Verbindung. Ein neues auf Nickel basierende Hydrid der Zusammensetzung $La_2MgNi_2H_8$ wurde entdeckt und hinsichtlich Struktur und Eigenschaften aufgeklärt. Die Verbindung ist nichtmetallisch und enthält die ersten in der Literatur bekannten dinuklearen $[Ni_2H_7]^{7-}$ and tetranuklearen $[Ni_4H_{12}]^{12-}$ Komplexe. Der Wasserstoff-induzierte Metall-Isolatorübergang in diesem System ist von prinzipiellem Interesse, für mögliche Anwendungen ist das System jedoch nicht genügend reversibel. Die Palladiumverbindung $LaMg_2PdH_7$ ist eine neues *d*-Metallhydrid welches $[PdH_4]^{4-}$ Komplexe enthält, und ebenfalls einen Wasserstoff-induzierten Metall-Isolatorübergang zeigt. Im Vergleich zur Nickelverbindung ist dieses System unter technisch relevanten Bedingungen reversibel und daher für Anwendungen, wie z.B. Wasserstoffdetektoren, von Interesse. Nach langjährigen Bemühungen ist es uns gelungen, das *p*-Metallhydrid $Mg(BH_4)_2$ mittels einer neuartigen synthetischen Methode unter guter Ausbeute zu präparieren. Die Verbindung hat eine theoretische Wasserstoffspeicherkapazität von >10 wt.%, gibt den Wasserstoff allerdings erst bei über 150℃ ab. Ihre Struktur ist markant verschieden von jener der analogen Kalziumverbindung $Ca(BH_4)_2$ und zeigt eine äusserst komplexe Anordnung von zehn Symmetrieunabhängigen $[BH_4]^-$ Anionen. Die Schwingungsdynamik der Rheniumverbindung $BaReH_9$ wurde durch inelastische Neutronenbeugung gemessen um jene Faktoren zu eruieren, welche die unbekannte Manganverbindung '$MgMnH_9$' möglicherweise stabilisieren könnte. Diese Verbindung würde, falls sie thermodynamisch stabil ist, den Rekord der Wasserstoffspeicherdichte in *d*-Metallhydriden brechen.

Projekt 101812, Klaus Yvon, Université de Genève

Abstract

Solid state metal hydrides provide the most energy efficient, compact and safe way of storing hydrogen. We have synthesized and investigated the following complex and *d*- and *p*- metal hydrides to be used in PEM fuel cell systems. The relatively inexpensive magnesium-iron compound Mg_2FeH_6 has been prepared by ball milling with a yield of 91% which sets a new record compared to the previously achieved yield of 80%. In order to decrease its thermal stability and increase its desorption kinetics, it was doped with a few at.% of $TiCl_3$ and Nb_2O_5. The experiments confirm the beneficial influence of doping on desorption kinetics, at least at the beginning of the desorption reaction, but show that the thermal stability is nearly unaffected. On the other hand, milling over longer time periods increases the equilibrium plateau pressure by ~0.1 bar, i.e. it destabilizes the compound. A new nickel based hydride of composition $La_2MgNi_2H_8$ has been discovered and characterized with respect to structure and properties. It is non-metallic and displays the first dinuclear $[Ni_2H_7]^{7-}$ and tetranuclear $[Ni_4H_{12}]^{12-}$ complexes known in the literature. Its hydrogen induced metal-insulator transition is of interest for hydrogen related devices such as hydrogen detectors, but it lacks reversibility. The palladium based compound $LaMg_2PdH_7$ is a new *d*-metal hydride that contains $[PdH_4]^{4-}$ complexes and shows a hydrogen induced metal-insulator insulator transition. Compared to the nickel compound it is reversible under technically useful conditions and thus of interest for practical applications such as hydrogen detectors. After some years of efforts, the *p*-metal hydride $Mg(BH_4)_2$ has been prepared by a new synthetic method. The compound desorbs hydrogen above 150°C and has a theoretical hydrogen storage capacity of >10 wt.%. Its structure differs significantly from the calcium analogue $Ca(BH_4)_2$ and displays a very complex arrangement of ten symmetry independent $[BH_4]^-$ anions. Raman data are available to understand better the dynamics of the system. The dynamics of rhenium based $BaReH_9$ has been investigated by neutron scattering techniques in order to better understand the factors that could possibly stabilize the manganese analogue '$MgMnH_9$'. The latter hydride, if thermodynamically stable, is expected to display new record hydrogen storage efficiencies among complex *d*-metal hydrides.

1. Ausgangslage

Hydrogen storage constitutes a major unsolved problem in a future hydrogen economy, in particular for the use of PEM fuel cell systems. In order to enable industrial commercialization of hydrogen fuel cell vehicles, for example, efficient and cost effective on-board hydrogen storage systems are mandatory. In spite of considerable R&D efforts in most industrialized countries, in particular the EU, the US and Japan, such systems do not yet exist. This is due to the difficulties in meeting the system targets set up in various countries (e.g. US DoE) and the fact that, up to date no system anywhere in the World meets on-board requirements as defined by industry. Current on-board hydrogen storage technologies rely mainly on classic approaches such as compressed hydrogen gas (CGH2) and cryogenic (liquid) hydrogen (LH2), whereas solid hydrogen stores (metal hydrides) tend to loose momentum because progress on the materials side is considered slow. Yet, compared to current fossil fuel technologies all three storage approaches suffer from technical and economic shortcomings, and this situation will presumably prevail until new breakthroughs are achieved.

In the recent past, hydrogen storage has made significant technical progress, including in the solid state. Considering system capacity, ~4.5 wt.% (~2.4 kg H2/100 l) are achievable for CGH2 storage and ~14 wt.% (~4 kg H2/100 l) for LH2 storage, whereas for reversible solid storage at room temperature ~1.8 wt.% (alanates) is state of the art, and higher values are achievable for temperatures of interest for PEM fuel cell applications (80°-100°C). Ho wever, in spite of this progress, none of the storage routes investigated (liquid, gaseous, and solid) meets the targets necessary for successful commercialisations, neither for on-board nor for off-board storage applications. Major bottlenecks include system capacity, safety, storage losses, permeability, energy losses, tank design, heat management, recycling of materials and last but not least costs. Clearly, what type of hydrogen storage method is most suitable for what particular application it still an open question. While progress for LH2 concerns mainly the design of compact, light and free-form tanks, the issues of energy penalty (liquefaction), storage losses (boil-off, permeability) and costs need to be addressed in more detail. Compressed gas tanks reaching 700 bar hydrogen pressure appear to be state of the art, but concern persists concerning safety (aging, fatigue, failure, burst, permeability of liners), energy loss (compression needs energy, cold filling needs instalment of an heat exchanger), environment (recyclable materials), costs (in particular for composite structures) and certification. Finally, solid storage, which is the safest and most energy saving method, does not yet meet technical and economic criteria, in particular for mobile applications (weight, cyclability, operation temperature, kinetics, material cost).

2. Ziel der Arbeit

The project aimed at the synthesis of new complex *d*- and *p*- metal hydrides to be used with PEM fuel cell systems. The IEA target properties of such materials are hydrogen dissociation temperatures of less than 80℃ at 1.5 bar pressure, and hydrogen/metal weight ratios of more than 5 wt.%.

4. Ergebnisse

The following *d*- and *p*-metal hydrides have been investigated in conformity with the project plan:

Mg_2FeH_6: This complex *d*-metal hydride is relatively inexpensive and fulfills the weight efficiency target of IEA Task 22 (> 5 wt.%), but not the temperature/pressure target (desorption temperature ~300℃ at 1 bar hydrogen pressure, compared to a target of > 80℃). In order to decrease the desorption temperature (or increase the equilibrium pressure) "catalyzed" desorption experiments were performed on samples containing either $TiCl_3$ or Nb_2O_5 as "catalysts" (called "dopants" thereon). The samples were prepared by using the ball milling ("mechanical alloying") method in collaboration with E. Rönnebro (*Sandia Lab.* USA) who participates in the IEA task 22 project. The best sample contained 91% of Mg_2FeH_6 which sets a new record compared to the previously achieved yield of 80%. As shown in Table 1 for 4 selected samples, two types of starting mixtures and milling times were used, one involving elemental Mg and Fe, and a milling time of 4 hours (samples 4 & 5) and the other involving magnesium hydride and Fe, and a milling time of 20 hours (samples 6 & 7). The dopants used were either $TiCl_3$ (sample 6) or Nb_2O_5 (sample 7).

***Table 1**: Educts, nominal composition, dopants and milling times*

	educts/nominal composition	Dopant (at.%)	milling time
Sample 4	3Mg + Fe	-	4h
Sample 5	3Mg + Fe	4% $TiCl_3$	4h
Sample 6	3MgH_2 + Fe	-	20h
Sample 7	3MgH_2 + Fe	2% Nb_2O_5	20h

After milling, the samples were sintered at 370ºC under 700 bar hydrogen pressure, and then analyzed by X-ray diffraction (XRD) and thermal desorption.

a) XRD results: As shown in Table 2 all samples contain as majority phase Mg_2FeH_6 and various amounts of unreacted Fe and MgH_2, and some MgO.

***Table 2** : phase quantification by XRD of samples before thermal desorption measurements*

	Mg_2FeH_6	MgH_2	Fe	MgO
Sample 4	72%	20%	7%	1%
Sample 5	66%	23%	9%	2%
Sample 6	84%	6%	5%	5%
Sample 7	76%	10%	1%	13%

The highest yields for the Mg_2FeH_6 phase were obtained with MgH_2 + Fe as educts, and by using long milling times (samples 6 & 7), whereas lower yields were obtained with Mg + Fe as educts and short milling times (samples 4 & 5). Crystalline domain size and lattice strain of the Mg_2FeH_6 phase were extrapolated from "*Williamson-Hall plots*" by using equation (1).

$$\beta.\cos\theta = \lambda/D + 4\,\varepsilon\,\sin\theta \qquad (1)$$

where β = full width at half-maximum of diffraction peaks, D = average crystalline domain size, λ = XRD wavelength, ε = average lattice strain, and θ = diffraction angle.

As shown in Table 3, domain size in the samples covers the range 500 - 1600 Å, and lattice strain the range 0.25 – 0.70 %. As expected, both quantities depend on milling time, i.e. long milling times decrease grain size and increase lattice strain.

***Table 3** : Average crystalline domain size and lattice strain from Williamson-Hall plot on XRD data*

	Average domain size (Å)	Average lattice strain
Sample 4	1557.9(2)	0.003298(1)
Sample 5	1553.3(5)	0.002515(1)
Sample 6	469.0(3)	0.004966(3)
Sample 7	820.4(2)	0.007041(3)

b) Thermal desorption analysis results: Pressure-composition-isotherms (PCT) were recorded in order to determine the influence of dopants on thermodynamics and kinetics. All measurements were done at 300℃ and during hydrogen desorption. As shown in Figure 1, all samples except one (sample 6) display two "plateau regions" (i.e. hydrogen equilibrium pressures), one at high pressure (1 - 1.5 bar) corresponding to the decomposition of the less stable binary hydride MgH_2, and another at low pressure (0.5. - 0.8 bar) corresponding to the decomposition of the more stable ternary hydride Mg_2FeH_6.

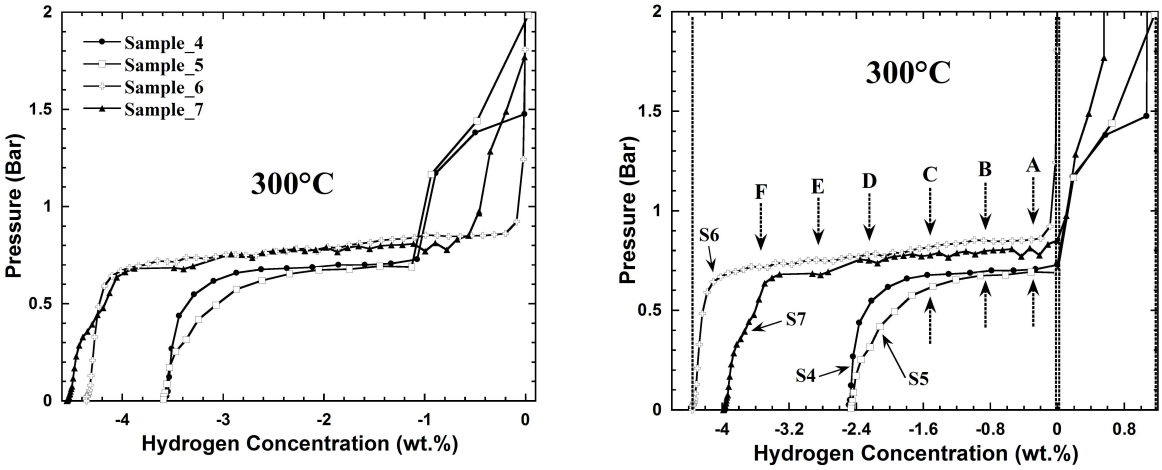

***Figure 1**: Pressure-composition isotherms upon desorption at 300℃; original unscaled data (left); data scaled according to hydrogen content at plateau region between Mg_2FeH_6 and MgH_2 (right)*

Interestingly, the largest influence on the plateau pressure appears to be the milling time. Long milling times (20 hours, samples 6 & 7) increases the equilibrium plateau pressure compared to short milling times (4 hours, samples 4 & 5), and this regardless of the nature of the dopant. The difference is ~0.1 bar, i.e. milling has a significant destabilizing influence on ternary Mg_2FeH_6. This tendency is in line with results obtained very recently on binary MgH_2 and ternary Mg_2NiH_4 as cited by Sakintuna et al. (*Int. J. of Hydrogen Energy 2007, 32, 1121-1140*). The pressure for hydrogen desorption of milled MgH_2, for example, is higher by 1.5 bar compared to that of the milled one. On the other hand, the presence and nature of dopants influence only little thermodynamics. In contrast to *p*-metal hydrides their presence decreases slightly the plateau pressure (by 0.02 bar for $TiCl_3$, by 0.05 bar for Nb_2O_5), i.e. the dopants tend to stabilize the Mg_2FeH_6 phase.

The reaction kinetics was investigated by measuring the evolution of hydrogen pressure as a function of time. For the sake of comparison, the data were analyzed such that they refer to definite regions in the PCT diagram (see letters A,B,C etc, and arrows in right part of Figure 1). Of particular interest are the data in the regions between the beginning of desorption of Mg_2FeH_6 and the end of desorption of MgH_2 (see point A), and further along the desorption plateau of Mg_2FeH_6 (see points B, C, D etc). As shown in the left part of Figure 2, the presence of dopants has a positive effect on desorption kinetics (faster kinetics for samples 5 and 7 compared to undoped samples 4 and 6) at the beginning of desorption (point A). Clearly, the effect is bigger for long-time milled samples than for short-time milled samples. However, as shown in the right part of Figure 2, this trend inverses as desorption of Mg_2FeH_6 proceeds (point B), i.e. the presence of dopants starts to have a detrimental effect on desorption kinetics (slower kinetics for doped samples 5 and 7 compared to undoped samples 4 and 6). This trend continuous along the plateau (points C, D, E etc, graphs not shown). The reason for this unexpected behavior is not clear.

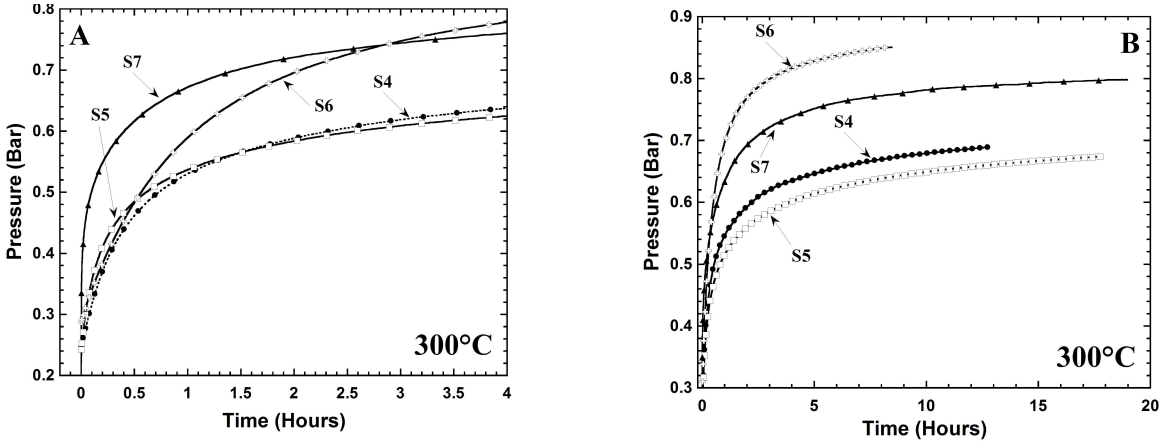

***Figure 2**: Desorption kinetics on points A (left) and B (right) of Mg_2FeH_6 plateau pressure*

In conclusion, ball milling of Mg_2FeH_6 has definitely a positive influence on its thermodynamics and kinetics. It increases the plateau pressure by ~0.1 bar, i.e. it destabilizes the compound, and it increases the speed of hydrogen desorption, at least at the beginning of the reaction. On the other hand, the role of the dopants, if any, is less clear. Finally, the influence of particle size and lattice strains on thermodynamics and kinetics is far from being understood.

La-Mg-Ni-H system: As we have anticipated, this system not only contains the recently reported complex *d*-metal hydride $LaMg_2NiH_7$ but also a great variety of other complex metal hydrides. Among these, one has now been characterized. It has the composition $La_2MgNi_2H_8$ and is the first hydride containing polynuclear hydride complexes based on a 3*d*-metal. In contrast to the known nickel based metal hydrides containing exclusively mononuclear tetrahedral $[NiH_4]^{4-}$ complexes with terminal hydrogen ligands, $La_2MgNi_2H_8$ displays both dinuclear $[Ni_2H_7]^{7-}$ and tetranuclear $[Ni_4H_{12}]^{12-}$ complexes with terminal and bridging H ligands (see Figure 3). The complexes are isolated from each other and are fully ordered.

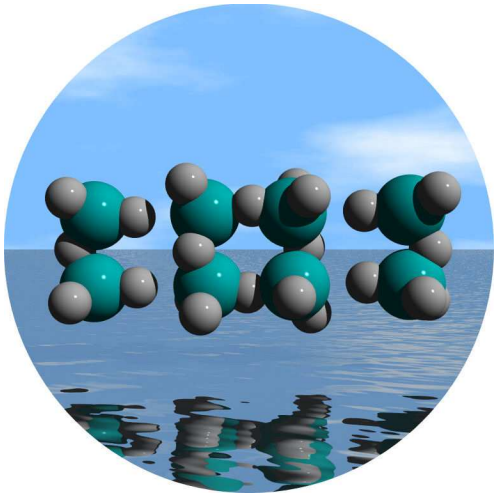

***Figure 3**: Dinuclear $[Ni_2H_7]^{7-}$ and tetranuclear $[Ni_4H_{12}]^{12-}$ complexes in $La_2MgNi_2H_8$ (Ni atoms in greenish blue, hydrogen atoms in grey); from [1].*

In view of its high materials costs the La_2MgNi_2-H system is less useful for large scale hydrogen storage applications. However, it is of major interest for its hydrogen induced metal-to-nonmetal transi-

tion. Four such transitions have been characterized so far in Geneva. They lead from the metallic compounds Mg_2Ni, Mg_3Ir, $LaMg_2Ni$ and La_2MgNi_2 to the non-metallic, colored hydrides Mg_2NiH_4 (brownish-red), $Mg_6Ir_2H_{11}$ (red), $LaMg_2NiH_7$ and $La_2MgNi_2H_8$ (dark grey), respectively. The transitions are not always reversible, but of considerable fundamental and technological interest. Not only do they contribute in shedding new light on the metal hydrogen interactions on the frontier between covalently bonded and metallic systems, but they also provide the active principle of hydrogen related devices such as 'optical mirrors' (for example Mg_2Co-H), and hydrogen detectors. Such applications, however, require that one succeeds in making these systems more reversible at useful temperatures. Details about the La_2MgNi_2-H system have been published [1], and a review on related systems has appeared in print [2]. The aim of our future work is to replace Ni in La_2MgNi_2 by cheaper transition elements such as Cu and Fe and to make the system more reversible.

'$MgMnH_9$' : This compound, if thermodynamically stable, is expected to display a new record hydrogen storage efficiency among complex *d*-metal hydrides (~9 wt.%). In order to better understand the factors that could possibly stabilize its structure, we have measured the dynamics of the rhenium analogue $BaReH_9$ by neutron scattering, and comparing the results with theoretical spectra as calculated by density functional theory (collaboration with Dr. S.F. Parker, ISIS, Rutherford, UK). The results show that the bonding between the Re and the H is relatively weak and largely covalent, while that between Ba and H is dominated by relatively strong, long-range Coulomb interactions. Thus the counter ion is crucial for the stability of the hydride, and varying it potentially offers a method to fine tune its properties [3]. Synthesis attempts of $MgMnH_9$ have not been successful yet.

$LaMg_2(Ni,Pd)H_7$: In this system, attempts were made to replace nickel partially or completely by palladium in order to improve the reversibility of the hydrogen induced metal-insulator transition in the previously investigated $LaMg_2Ni$-H system. We have succeeded in replacing Ni totally by Pd, thus obtaining the new complex *d*-metal hydride $LaMg_2PdH_7$. While the latter is not suitable for large scale hydrogen storage applications it is of major interest for its hydrogenation induced metal-insulator transition. As shown in Figure 4, $LaMg_2Pd$ is metallic while the complex *d*-metal hydride $LaMg_2PdH_7$ is insulating. This is due to the localization of conduction electrons into Pd-H bonds of $[PdH_4]^{4-}$ complexes in the structure. In order to shed light on the M-I transition we have investigated the hydride more closely upon desorption. Surprisingly, the desorption does not proceed directly from the full hydride $LaMg_2PdH_7$ to the hydrogen free intermetallic compound $LaMg_2Pd$, but goes over an intermediate hydride phase of composition $LaMg_2PdH_{\sim 3}$. PCT and diffraction data show that its formation is accompanied by a relatively small hysteresis and practically no degradation. The fact that the M-I transition is reversible and occurs over a smaller H concentration range than anticipated (3 versus 7 H atoms/formula unit) is an advantage for technological applications such as in hydrogen detectors because it decreases materials degradation due to hydrogen induced volume changes. Work is in progress to model the M-I transition theoretically in collaboration with M.Y. Chou (*Georgia Institute of Technology, Atlanta, USA*). A scientific paper on this system has appeared in press [4] and another is in preparation.

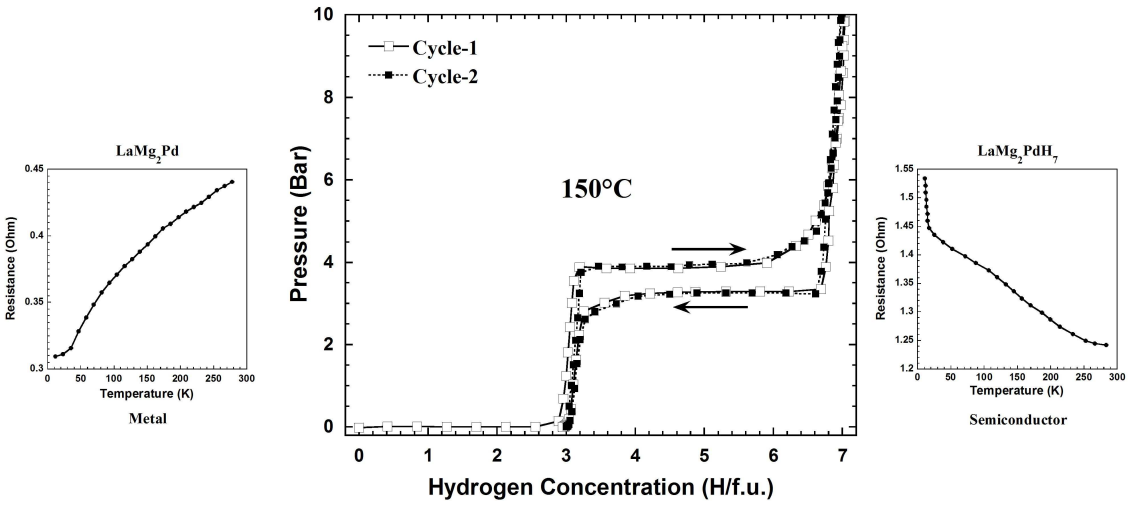

Figure 4 *: Electric resistance and hydrogen induced metal-insulator transition in $LaMg_2Pd$–H system; from [4].*

$\underline{Mg(BH_4)_2}$: This complex *p*-metal hydride has a theoretical hydrogen storage capacity of >10 wt.% and is of major interest for possible applications. Prior to our work it had not been characterized with respect to structure and hydrogen sorption properties. In collaboration with H. Hagemann (*University of Geneva*) we have obtained the compound by a hitherto unexplored synthetic method that avoids the use of diborane, according to reaction (1):

$$MgCl_2 + 2\,NaBH_4 \xrightarrow{Et_2O} Mg(BH_4)_2 + 2\,NaCl \qquad (1)$$

The reaction involves metathesis of $LiBH_4$ and $MgCl_2$ in diethyl ether which is more efficient than the previously reported reaction from $NaBH_4$ and $MgCl_2$ that yields a solvated product which is rather amorphous. We emphasize that drying up to 145°C was crucial for a complete removal of the solvent and obtaining a highly crystalline product suitable for high-resolution diffraction studies. The structure has been solved for the first time. It differs significantly from the calcium analogue $Ca(BH_4)_2$. It has hexagonal symmetry and displays 10 symmetry independent $[BH_4]^-$ anions that surround the Mg sites in tetrahedral configurations. In the meantime the structure has been confirmed by US scientists. The compound desorbs hydrogen above 150°C and has a theoretical hydrogen storage capacity of >10 wt.%. Thus it is of major interest for hydrogen storage applications provided it can be made more reversible. Raman data are available to understand better the dynamics of the system. Experiments to destabilize the compound have not yet started. A scientific paper has appeared in press [5].

$\underline{Li_4BN_3H_{10}}$: This promising *p*-metal hydride has been characterized for the first time in Geneva at the beginning of the project [6], but work on it has been interrupted because suitable samples containing dopants such as $TiCl_3$ were not supplied by the industrial partner.

Publications: The project has lead to a dozen scientific publications that appeared in refereed journals of high international standard and impact, such as *Angewandte Chemie, Int. Ed*. and *Inorganic Chemistry*, including a review on *d*-metal complexes (publications No. 1-11, see list below). Two more papers are in progress.

5. Diskussion

In spite of some operational delay, satisfactory progress has been made. In particular, the following milestones have been met: the synthetic yield of ball-milled Mg_2FeH_6 (> 80%) has been increased and the hydride has been destabilized by ball-milling; furthermore, the positive influence of doping on kinetics of this hydride, in particular at the beginning of the decomposition reaction has been ascertained. A new quaternary metal hydride of composition $La_2MgNi_2H_8$ has been discovered in the La-Mg-Ni-H system that shows the first polynuclear *3d* metal hydride complexes and a hydrogen induced metal-insulator transition that could be of interest for hydrogen related devices. Almost full reversibility of the hydrogen induced metal-insulator transition in the $LaMg_2$(Ni,Pd)-H system has been achieved at 150°C, thus paving the way for its possible application in hydrogen detectors. The extremely light hydrogen storage material $Mg(BH_4)_2$ has been synthesized successfully and characterized with respect to structural and spectroscopic properties. The compound desorbs hydrogen above 150°C and has a theoretical hydrogen storage capacity of >10 wt.%. Thus it is of major interest for hydrogen storage applications provided it can be made more reversible. On the other hand, the following milestones have not been met: synthesis of the elusive *d*-metal hydride $MgMnH_9$, and decrease of hydrogen desorption temperatures of $Li_4BN_3H_{10}$ and $Mg(BH_4)_2$.

6. Schlussfolgerungen

While the IEA weight target for hydrogen storage in PEM fuel cell systems has been met (hydrogen/metal weight ratios > 5 wt.%) the thermal stability target (hydrogen dissociation temperatures < 80°C at 1.5 bar pressure) has not been reached. On the other hand, new materials have been discovered that are of interest in related devices such as hydrogen detectors. Thus, for the years 2008/2009 we are planning to destabilize Mg_2FeH_6 further by ball milling (collaboration with SANDIA), to investigate the hydrogen induced metal-insulator transition in thin films of $LaMg_2Pd$ (collaboration with National Project MANEP), to push forward the synthesis of the elusive *d*-metal hydride $MgMnH_9$, to continue substitutions in the La-Mg-Ni-H system, and to destabilize the *p*-metal hydrides $Li_4BN_3H_{10}$ (collaboration with Industry) and $Mg(BH_4)_2$ (collaboration with EMPA). Future work will also include the study of so-called "*bcc alloys*" to understand their poor cycling stability (collaboration with Jap. Metal & Steels Co.) and the study of chemical hydrides such as AlH_3 (collaboration with Brookhaven National Labs). Another challenge for future work is to explore 3*d* metal-hydrogen systems, in particular those

likely to display polynuclear and/or possibly heteronuclear complex anions that are fully reversible. The prospects of finding such complexes are good, since the possible element combinations are numerous and not yet fully explored.

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