



PROJEKTTITEL

NEW METAL HYDRIDES FOR HYDROGEN STORAGE IN FUEL CELL SYSTEMS

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ZUSAMMENFASSUNG

Solid state metal hydrides provide the most compact and safe way of storing hydrogen. During this year we have investigated the following complex *d*- and *p*- metal hydrides to be used with PEM fuel cell systems. Mg_2FeH_6 has been prepared with a yield of 91% which sets a new record compared to the previously achieved yield of 80%. Catalyzed desorption experiments confirmed the beneficial influence of dopants such as $TiCl_3$ on its desorption kinetics. The dynamics of $BaReH_9$ has been investigated by neutron scattering techniques in order to better understand the factors that could possibly stabilize the manganese analogue 'MgMnH₉'. The latter compound, if thermodynamically stable, is expected to display new record hydrogen storage efficiencies among complex *d*-metal hydrides. A new 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. The hydrogen induced metal-insulator transition is of interest for of hydrogen related devices such as 'optical mirrors' and hydrogen detectors. $LaMg_2PdH_7$ is a new complex d-metal hydride which is also insulating. Compared to its nickel analogue $LaMg_2NiH_7$ it is partially reversible under technically useful conditions and thus of interest for practical applications. The structure of the *p*-metal hydride $Mg(BH_4)_2$ has been solved. It displays ten symmetry independent $[BH_4]^-$ anions. The compound desorbs hydrogen above 150°C.

Projektziele

The project aims 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°C at 1.5 bar pressure, and hydrogen/metal weight ratios of more than 5 wt. %.

Durchgeführte Arbeiten und erreichte Ergebnisse

Since the beginning of this project (February 2006) the following complex *d*- and *p*-metal hydrides have been investigated in conformity with the project plan:

Mg₂FeH₆: This complex *d*-metal hydride is relatively inexpensive and fulfills target A of IEA Task 17 (weight efficiency > 5 wt.%), but not target B (desorption temperature > 80°C at 1 bar). Catalyzed desorption experiments confirmed the beneficial influence of dopants such as TiCl₃ on its desorption kinetics. Consequently, new synthesis attempts by using a novel route were conducted in collaboration with E. Ronnebro (*Sandia Lab.* USA) who participates in the IEA task 22 project. Various starting mixture were used, such as 3MgH₂+Fe or 3Mg+Fe, and these were milled for 4 to 20 hours with and without TiCl₃ added as a catalyst. The pre-formed Mg₂FeH₆ was then hot sintered at 700 bar and 370°C. Six of these samples have been investigated in Geneva with respect to their phase composition, lattice strain and pressure-composition-isotherms (PCT). The results obtained are encouraging. All samples contained as majority phase Mg₂FeH₆ and various amounts of Fe and MgH₂. The best sample (starting mixture 3MgH₂+Fe, no catalyst, milling time 20 hours) contained 91% of Mg₂FeH₆ which sets a new record compared to the previously achieved yield of 80%. Lower yields were obtained when the starting mixture consisted of 3Mg+Fe and the milling time was 4 hours. As expected the X-ray analysis showed that the lattice strain scales with the milling time. PCT measurements have been performed, but the values obtained for the equilibrium pressures are not reliable because of the formation of MgO during the measurements. The origin of this unwanted by-product is currently under investigation.

La-Mg-Ni-H system: As we have predicted, this system not only contains the recently reported complex *d*-metal hydride LaMg₂NiH₇ but also a great variety of other complex metal hydrides. Among these, one has now been characterized. It has the composition La₂MgNi₂H₈ 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 [NiH₄]⁴⁻ complexes with terminal H ligands, La₂MgNi₂H₈ displays both dinuclear [Ni₂H₇]⁷⁻ and tetranuclear [Ni₄H₁₂]¹²⁻ complexes with terminal and bridging H ligands (see figure 1).

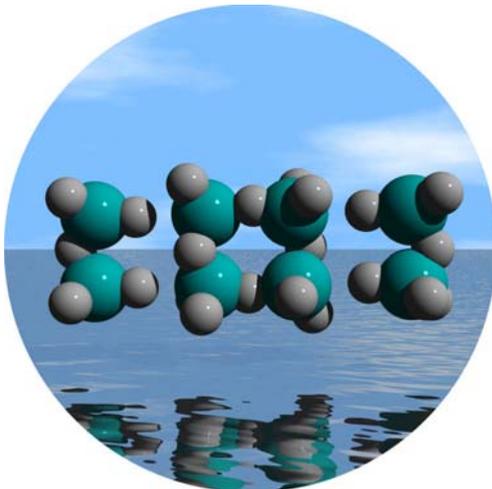


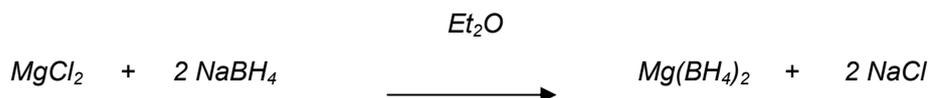
Figure 1: Dinuclear [Ni₂H₇]⁷⁻ and tetranuclear [Ni₄H₁₂]¹²⁻ complexes in La₂MgNi₂H₈ (Ni atoms in greenish blue, hydrogen atoms in grey blue)

The complexes are isolated from each other and are fully ordered. Interestingly, the hydride is non-metallic and thus provides the fourth example of a hydrogenation induced metal-to-nonmetal transition in transition metal-hydrogen systems. The transitions lead from a metallic compound (Mg₂Ni, Mg₃Ir, LaMg₂Ni, La₂MgNi₂) to a non-metallic hydride (brownish-red Mg₂NiH₄, red Mg₆Ir₂H₁₁, dark grey LaMg₂NiH₇ and La₂MgNi₂H₈), but are not always fully reversible. They are of both 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 Mg₂Co-H), and hydrogen detectors. This requires, however, that one succeeds in making these systems more reversible at useful temperatures (publication 1).

'MgMnH₉': 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 finished measuring the dynamics of the rhenium analogue BaMnH₉ 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 (publication 2).

LaMg₂(Ni,Pd)H₇: Attempts have been 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 LaMg₂Ni-H system. We have now succeeded in replacing Ni totally by Pd, thus obtaining the new complex **d**-metal hydride LaMg₂PdH₇. As expected, the hydride is insulating. Furthermore, in contrast to the nickel system, it is at least partially reversible under technically useful conditions and thus of greater use for practical applications (publication 3).

Mg(BH₄)₂: This complex **p**-metal hydride has a theoretical hydrogen storage capacity of >10 wt.% and thus 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 Dr. H. Hagemann (*University of Geneva*) we have now succeeded in preparing this compound according to the reaction



In contrast to the relatively low yield achieved during our preliminary work (~50%), we have obtained yields close to 90%, including for the deuteride. The most challenging part of the work was the preparation of deuteride samples for neutron diffraction, because deuterated educts of sufficient purity were not easily obtainable. The samples obtained were sufficiently well crystallized to be investigated by synchrotron and neutron powder diffraction. The structure has been solved and is currently under refinement. It has hexagonal symmetry and displays 10 symmetry independent [BH₄]⁻ anions. This compound is stable up to 150°C. Raman spectra are also available.

Li₄BN₃H₁₀: Work on this promising **p**-metal hydride has not yet resumed because suitable samples containing dopants such as TiCl₃ have not been supplied by the industrial partner (General Motors, USA)

"Milestones":

We have met the milestones of the project as foreseen for the 1st year: preparation of new hydrogen storage materials in the La-Mg-Ni-H system showing polynuclear **3d** metal hydride complexes and/or hydrogen induced metal-insulator transitions; increasing the yield of ball-milled Mg₂FeH₆ (> 80%); synthesis of the deuteride Mg(BD₄)₂ with yields greater than 50% for structural investigations. For the second year we foresee to achieve reversibility of the hydrogen induced metal-insulator transition in the LaMg₂(Ni,Pd)-H system; to decrease the desorption temperature of Mg₂FeH₆ to less than 200°C by doping with TiCl₃; to synthesize MgMnH₉ by ball milling; to characterize fully Mg(BH₄)₂ by measuring structural, thermodynamic and spectroscopic properties; and to decrease the desorption temperature of Li₄BN₃H₁₀ to less than 250°C by either adding dopants such as TiCl₃, or partially replacing [BH₄]⁻ complexes by [NH₂]⁻ complexes.

Nationale Zusammenarbeit

The project has benefited from collaborations with Dr. H. Hagemann (*University of Geneva*) and discussions with Dr. A. Züttel (*EMPA*), and from equipment and manpower from, and advice by members of, the *Paul-Scherrer Institute* (Villigen) for scattering experiments (*SINQ*, *SLS*). The collaborations were extremely fruitful und essential for the project. Funding by the *Swiss National Science Founda-*

tion and the University of Geneva has allowed to project to start in the absence of a financial contribution by the Swiss Federal Office of Energy.

Internationale Zusammenarbeit

The project is about to be re-integrated into the *International Energy Agency* (IEA) agreement on the production and utilisation of hydrogen; Task 22 : 'Fundamental and Applied Hydrogen Storage Materials Development' (operating agent Prof. B. Hauback). The task targets are A: Develop a reversible or regenerative hydrogen storage medium fulfilling international targets for hydrogen storage; B: Develop the fundamental and engineering understanding of hydrogen storage by various hydrogen storage media that have the capability of meeting target A; C: Develop hydrogen storage materials and systems for use in stationary applications. Given that the present project focuses on PEM fuel cell systems the materials to be developed should be capable of 5 wt.% hydrogen capacity with a dehydriding temperature of less than 80°C at 1 bar hydrogen pressure absolute (IEA Task 17 target). The collaborations resulting from this international effort have allowed us to interact with researchers across the world, such as Dr. E. Rönnebro (*SANDIA, Livermore, USA*) for the synthesis of *d*-metal hydrides such as Mg₂FeH₆, M.Y. Chou (*Georgia Institute of Technology, Atlanta, USA*) for theoretical modeling, and Dr. S Parker (*ISIS, Rutherford, UK*) for spectroscopic measurements.

Bewertung 2006 und Ausblick 2007

During this year, our work has lead to 8 scientific publications of which 4 have been, or are about to be submitted to refereed journals of high international standard such as Physical Review Letters, Angew. Chem. Int. Ed, Inorganic Chemistry etc (see list below). A challenge for future work is to investigate more **3d** 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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