European Workshop on Hydrogen Storage Technologies

co-organized by NESSHY, NANOHY, and FLYHY EC projects

University of Salford – Manchester, UK
Wednesday, 13 January 2010

Location: Room G14 - Lady Hale Building, University of Salford

Program

09:00-09:10	Welcome - Introduction	Th. Stubos NCSR "Demokritos"
09:10-09:30	Effect of Anion Substitution in MgH_2/borohydride based Reactive Hydride Composites (FLYHY)	M. Dornheim GKSS
09:30-09:50	Halogen substituted metal borohydrides for hydrogen storage (FLYHY)	T.R. Jensen U. Aarhus
09:50-10:10	Fluorine substitution in alane? (FLYHY)	B. Hauback IFE
10:10-10:30	Diborane - The key to reversible hydrogen storage in borohydrides (NESSHY)	O. Friedrichs EMPA
10:30-10:50	Properties of the Li-N-H system (NESSHY)	I. Morisson U. Salford
10:50-11:10	*Coffee break*	
11:10-11:30	Thin Film Light-weight Complex Metal Hydrides (NESSHY)	B. Dam VU/TU Delft
11:30-11:50	From thin film to bulk: the hydrogenation properties of Mg:Ni:Ti 69:26:5 (NESSHY)	R. Domènech-Ferrer IFW
11:50-12:10	Physisorption of hydrogen on novel nanoporous materials (NESSHY)	M. Hirscher MPI
12:10-12:30	Computational study of hydrogen storage in metal-doped graphitic materials (NESSHY)	G. Froudakis Th. Steriotis U. Crete/NCSRD
12:30-14:00	*Lunch break*	
14:00-14:20	Impact of stress density via ECAP and role(s) of early TM additives on the hydrogenation parameters of magnesium (NESSHY)	D. Fruchart CNRS
14:20-14:40	Medium Temperature Hydrogen Storage Tank activities (NESSHY)	J. Bellosta von Colbe GKSS
14:40-15:00	Nano-confined metal hydride composites: Synthesis, characterization, and sorption properties (NANOHY)	A. Roth FZK
15:20-15:40	In situ Raman and neutron spectroscopy of complex hydrides (NANOHY)	L. Ulivi CNR
15:40-16:00	Small-angle scattering investigations of Mg-borohydride infiltrated in activated carbon (NANOHY)	S. Sartori IFE
16:00-16:30	Discussion	ALL
16:30	End of Workshop	

Abstracts

FLYHY presentations

Effect of Anion Substitution in MgH_2/borohydride based Reactive Hydride Composites

Martin Dornheim[a], Karina Suarez[a], José Bellosta von Colbea[a], Klaus Taube[a], Torben Jensen[b], Pablo Arnal[c], José Ramallo Lopez[c]

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Reactive Hydride Composites like combinations of MgH_2 with $M(BH_4)_x$ (M being Li, Na or Ca) show significantly reduced values of reaction enthalpies as well as improved ab- and desorption kinetics compared to the pure borohydrides. Furthermore, due to their high reversible gravimetric storage capacities of up to 11 wt. % they are promising candidates for future hydrogen storage applications.
However, in spite of significantly lowered values of reaction enthalpy and thus a high thermodynamic driving force for desorption hydrogen release still takes place at temperatures above 250°C only.
Fluorine addition offers the possibility to fine tune reaction enthalpies of complex hydrides and hydride composites. In addition F- containing additives help to improve reaction kinetics of complex hydrides significantly. In this presentation we present recent results on the feasibility and effects of F-substitution in RHCs.

Halogen substituted metal borohydrides for hydrogen storage

Torben R. Jensen[a], Line Rude[a], Bo Richter[a], Bjørn C. Hauback[b], Hilde Grove[b], Magnus H. Sørby[b], Marcello Baricco[c], Martin Dornheim[c], José Bellosta von Colbe[d], Klaus Taube[d]

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Complex metal hydrides such as borohydrides, based on $BH\tilde{4}$, are currently of great interest as potential hydrogen storage materials, since they have high gravimetric hydrogen density and show a variety of decomposition temperatures. However no single material has yet been found, which fulfils all the criteria for mobile hydrogen storage.
It was found that a new substituted material, $Li(BH_4)_{1-x}Cl_x$, x ~ 0.1 to 0.4, can be prepared at relatively low temperatures, 110 < T < 250 °C below the melting point of the solids by diffusion of ions in the solid state. This reaction mechanism preserves the hexagonal $LiBH_4$ structure. The new substituted material, $Li(BH_4)_{1-x}Cl_x$, is stable upon cooling to RT and shows a similar phase transition to an orthorhombic phase as observed for the pure $LiBH_4$. Structural analysis suggests that $\tilde{Cl}$ substitutes for the $BH\tilde{4}$ ion in the solid $LiBH_4$ material. This illustrates that anion substitution in borohydrides can be performed and suggests this approach as a mean for tailoring physical properties. In this talk the systems $LiBH_4$-LiX and $Ca(BH_4)_2$-CaX_2, X = $\tilde{F}$, $\tilde{Cl}$, $\tilde{Br}$ and $\tilde{I}$ will be discussed.

Fluorine substition in alane?

Bjørn C. Hauback[a], Jon Erling Fonneløp[a], Hilde Grove[a], Magnus H. Sørby[a], Marcello Baricco[b]

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The analogy between hydrides and fluorides with similar crystal structures has been known for several years. Recently, it has been found that the stability of complex hydrides also can be changed by substitution on the anion lattice, and the mixed hydride-fluoride $Na_3AlH_{6-x}F_x$ with x≈4 was prepared from NaF, Al and H_2 (> 60 bar). Pressure composition isotherms show a plateau pressure of about 25 bar for dehydrogenation at 120 °C compared to 1 bar for Na_3AlH_6, thus a significant destabilization.

Alane (AlH_3) with 10.1 wt% hydrogen takes at least 6 different structural modifications. α-AlH_3 is the most stable with reaction enthalpy of about -7.6 kJ/mol H_2. The compound is kinetically stable at room temperature. Furthermore alane is not reversible at moderate conditions. There are significant structural similarities between alane and the corresponding fluoride compounds. The goal has been to search for possible fluorine substitution in alane and furthermore to prepare a compound with higher stability and reversibility at moderate conditions.
The presentation will describe the efforts to synthesize fluorine substituted alane using different milling techniques under various conditions. Furthermore, results from theoretical modelling will be included in the presentation.

NESSHY presentations

Diborane - The key to reversible hydrogen storage in borohydrides

Oliver Friedrichs, Andreas Züttel

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Complex hydrides have been investigated as a potential future energy carrier, since 1997, when Bogdanovic et al. published on the catalytic effect of Ti on the hydrogen sorption of sodium alanate. In 2003, borohydrides ($M[BH_4]_x$) were proposed as new hydrogen storage materials . The gravimetric hydrogen density of some of these borohydrides, such as $LiBH_4$, exceeds even that of gasoline. However, the hydrogen absorption and desorption mechanism is not yet understood, and high pressures and temperatures are still required for hydrogen absorption. In contrast to the alanates, no catalyst has been discovered for the hydrogen sorption reaction of borohydrides.
In the present work, we show that diborane (B_2H_6) plays a key role in reversible hydrogen storage in borohydrides. We identified the crucial role of diborane in the formation and decomposition mechanism of borohydrides and present a model explaining the mass transport during these processes. Based on these insights, we developed a new method for the solvent-free synthesis of borohydrides at room temperature and demonstrated its feasibility with the synthesis of the following alkali and earth alkali borohydrides: $LiBH_4$, $Mg[BH_4]_2$, and $Ca[BH_4]_2$. This method makes possible the preparation of a wide range of different borohydrides, or even mixed borohydride systems, with tuneable sorption properties.

Properties of the Li-N-H system

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We present experimental and theoretical results to provide an understanding of the phase diagram of the Li-N-H system. Experimental characterisation studies include neutron diffraction studies to determine structure in stoichiometric and non-stoichiometric phases, incoherent inelastic neutron scattering studies to determine vibrational modes and quasi-elastic neutron scattering studies to determine diffusion rates. The experimental work is complemented by density functional calculations performed within the quasi-harmonic approximation used to determine phase stability and interpret the various neutron spectra. In addition, CALPHAD calculations of the Li-N-H phase diagram is presented as the predominance area phase diagram.

Thin Film Light-weight Complex Metal Hydrides

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Using Hydrogenography, we measure simultaneously the equilibrium pressure of hydride formation of thousands of materials on a single thin film wafer. This enables us to select the optimal composition for hydrogen storage in e.g. a ternary Mg-based sample. The ultimate goal of our project is to optimize and understand the hydrogenation properties of light-weight complex metal hydrides. For this we developed an in-situ reactive sputtering technique. It appears that the use of an additional atomic hydrogen source is essential to form $NaAlH_4$ by reactive sputtering. In this way we produce amorphous $NaAlH_4$ films at room temperature at a pressure of ~10^{-3} mbar. Due to the amorphous nature of the films we identify the alanate phase by IR spectroscopy. Annealing the film at 1 bar H_2 and 100 °C, we find that the films transform into NaH and Al, while segregating on a scale >> 200 nm. As a first step to identify the role of Ti we added metallic titanium to the film either after or during growth. No effect of these additives was found on the decomposition conditions nor the segregation behavior.

From thin film to bulk: the hydrogenation properties of Mg:Ni:Ti 69:26:5

C. Geipel, R. Domènech-Ferrer, C. Rongeat, O. Gutfleisch

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Gremaud et al. investigated a whole range of compositions in the ternary system Mg-Ti-Ni by hydrogenography technique. An enthalpy close to the desired value of 40kJ/mol H_2 has been found for Mg:Ti:Ni 69:26:5 thin films. The aim of this work is check whether it is feasible to obtain this kind of hydrogenation properties also in bulk samples.
Samples were prepared by high energy ball milling using a wide range of milling parameters: different atmospheres (high hydrogen pressure and argon), different temperature (ambient temperature and cryomilling), ball-to-powder ratios and rotational speed. In addition, melt spinning was performed to synthesise the compound.
Samples were analyzed by DSC and XRD techniques. XRD measurements indicated that there was no formation of any unknown hydride. Desorption temperature was measured by HP-DSC and compared with pure Mg_2NiH_4 hydride. DSC results showed that there was no significant reduction of the decomposition temperature as compared to Mg_2NiH_4. In summary, so far the hydrogenation properties observed in the thin films could not be reproduced in bulk samples.

Physisorption of hydrogen on novel nanoporous materials

Michael Hirscher, Barbara Schmitz, Ivana Krkljus, Kandavel Manickam

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The presentation will give an overview on hydrogen adsorption and desorption measurements of different novel nanoporous materials. For the maximum hydrogen uptake at high pressure and 77 K an almost linear correlation with the specific surface area is found, whereas, the adsorption at low pressure depends on the pore size or the chemical composition of the materials. Several experimental techniques have been applied to correlate the hydrogen uptake properties to the nanostructure of these novel materials. Maximum hydrogen storage capacity as well as heat of adsorption have to be considered to optimize the materials for their potential applications.

Computational study of hydrogen storage in metal-doped graphitic materials

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DFT modeling was used to understand the role of epoxide (C−O−C) and hydroxyl (C−OH) functional groups on the spillover mechanism for hydrogen storage on graphite oxide and oxygen-modified carbons. A primary spillover model was used, consisting of a Pt4 cluster, a graphite substrate model, and O and OH functional groups adsorbed on graphite. The spillover mechanism was found to proceed via the migration of dissociated hydrogen atoms from the Pt cluster to epoxide groups adjacent to the cluster (to form OH), followed by H migration by hopping on the adsorbed O atoms. The low energy barriers required for the relevant elementary steps indicate that the spillover process is facile when the carbon substrate is decorated with oxygen functionalities, leading to enhanced hydrogen uptake and faster charge/discharge kinetics. However, a reaction path was also identified, in which surface OH groups can react to form water, which can have adverse consequences for hydrogen storage on oxygenated carbons via spillover.

Impact of stress density via ECAP and role(s) of early TM additives on the hydrogenation parameters of magnesium

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It is of common knowledge that fast hydrogenation kinetics of Mg can be achieved, both realizing a high structure defect density and creating many interfaces with transition metal nano-particles. If ball milling (BM) is the reference method to process highly reactive MgH_2 powders according to the here above two considerations, Equal Channel Angular Pressing (ECAP) reveals an interesting tool since from many ajustable parameters, it allows to intersting results in terms of Severe Plastic Deformation (SPD), namely towards the maximum hydrogen uptake. The role of transition metal (TM) additives has been enlightened, thanks to the development of a nano-tank interfacing Nb to Mg thin layers on which in-situ X-rays experiments allow to point out some of the mechanisms involved in hydrogen diffusion at the Mg/TM interface. Also, syntheses under very high pressure experiments enable achieving the orthorhombic Mg~8-9TaHx. As for other parent Mg-TM-Hx ternaries, it is expected that two different bonding states for hydrogen can anticipate a marked destabilisation of the TM substituted cubic Mg superstructure.

Medium Temperature Hydrogen Storage Tank activities

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In the frame of the NESSHY Project, an improved medium temperature hydrogen storage tank based on sodium alanate is to be designed and built. In order to achieve this target, several activities have taken place. Studies directed to the use of compaction on the sodium alanate storage material have successfully shown good kinetics and capacity, almost indistinguishable from the loose powder. This opens the path to higher volumetric capacities than hitherto calculated, as well as improving the storage behaviour through better heat conductivity. An empirical kinetic model has been developed and validated for both the absorption and desorption of hydrogen in sodium alanate. The simulations carried out using this model are expediting the design of the NESSHY tank. Preliminary experiments using a small-scale pilot version of the NESSHY tank have shown promising sorption behaviour. Design activities have led to the preselection of materials for the optimized, lightweight hull of the NESSHY module. Experiments using the full-scale tank of the STORHY project have been started. Preliminary results indicate that these tests will be successfully finished on schedule.

NANOHY presentations

Nano-confined metal hydride composites: Synthesis, characterization, and sorption properties

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The idea behind the NANOHy project is to advantageously tune the sorption properties of complex metal hydrides by spatially confining the hydride particles in porous host materials.
Here we present examples of such nano-confined composites that have been synthesized in the course of the first two years of NANOHy. The systems are based on sodium alanate and magnesium borohydride, respectively, infiltrated into microporous activated carbons. These materials show significantly improved kinetics and, in case of the sodium alanate system, also indicate a change in its thermodynamic properties.

In situ Raman and neutron spectroscopy of complex hydrides

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The search of suitable hydrides for hydrogen storage can benefit from Raman and neutron spectroscopy, especially when it is possible to exploit these diagnostic techniques in situ, that is, in controlled conditions of gas pressure and temperature. In this way it is possible to observe and monitor phase transitions or sample chemical decomposition. In our laboratory we have studied the vibrational spectrum of several complex hydride compounds both at cryogenic temperature (15 K) and during or after thermal treatment at high temperature (up to 600 K), in a controlled atmosphere. In particular, in this talk I will present the results of the characterization of bulk samples of $Mg(BH_4)_2$ and AlH_3 where the proportions of the different phases can be changed by different thermal treatments. Additionally, both Raman and neutron spectra of Na_3AlH_6, recorded at low temperature, have disclosed the presence of low frequency lattice modes, that have been compared with computational results.

Small-angle scattering investigations of Mg-borohydride infiltrated in activated carbon

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In the present study $Mg(BH_4)_2$ and $Mg(^{11}BD_4)_2$ are infiltrated in pre-treated activated carbon and investigated with small-angle neutron scattering (SANS). The infiltration method is shown to be successful in modifying the size of the Mg-borohydride particles, as confirmed by scanning electron microscopy and x-ray diffraction data. The size of the particles for the infiltrated samples is estimated by SANS measurements to be mainly in the range <4 nm. The results suggest that the smallest pores of the scaffold are partially or fully filled and that this type of scaffold acts as an effective dispersing agent for Mg-borohydride.