PROJECT FINAL REPORT

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4.1 Final Publishable Summary Report

4.1.1 Executive summary

The work in NANOHy has dealt with theoretical modelling, synthesis, characterization, and testing of novel nanocomposite materials for hydrogen storage. Therefore, complex hydrides with high hydrogen content were infiltrated in nanoporous carbon materials which have been used as templates in order to produce a material where the hydride is finely dispersed in nanoscale voids which are separate from each other, thus preventing agglomeration of the nanoparticles and other unwanted side effects.

Fundamental physics and theoretical modelling predict an alteration of both kinetics and thermodynamics of the hydrides if particle sizes are in the lower nanometre range. Hence, it was the purpose of the project to produce appropriate composites with nanodispersed active material having altered properties with respect to working temperature and pressure, an enhanced reversibility, and controlled interaction between the hydride and the environment, leading to improved safety properties.

The composites developed in NANOHy were synthesized out of novel complex hydrides with very high hydrogen content and of nanocarbon templates. Alternatively, hydride colloids were coated in a Layer-by-Layer self-assembling process of dedicated polymers. Computational methods were used to model the systems and predict optimal materials/size combinations for improved working parameters of the systems. Sophisticated instrumental analysis methods were applied to elucidate the structure and the properties of the nano-confined hydrides. In addition, technical aspects were investigated such as the feasibility of an upscale of selected nanocomposite materials and their integration into a laboratory test tank.

NANOHy has achieved several scientific breakthroughs and has been an international leading activity in the field. It was shown for the first time that it is possible to infiltrate microporous scaffolds by complex hydrides and to change their properties: Considerable improvement of *kinetics* was noticed and all the nanoconfined hydrides exhibited considerably reduced dehydrogenation temperatures, especially the borohydrides. In the case of $Mg(BH_4)_2$ infiltrated in activated carbon a lowering of the desorption temperature was lowered by more than 120 K. In addition to the strong kinetic effects for the first time also *thermodynamic* effects were observed for complex hydrides and for MgH_2. The typical two-step plateau feature vanishes of the pressure-composition-isotherm of bulk catalyzed $NaAlH_4$ and is replaced by a sloped line between the charged and the discharged state which indicates a lack of intermediates and a multitude of states in the material. In the case of 1 nm MgH_2 particles a lowering of the enthalpy of formation was measured in the order of 11 kJ/mol. Related changes of the physical properties such as distribution of states, loss of crystal order in a nanoscale void were successfully predicted by theoretical modeling.

An upscale production of 500 g nanocomposite was performed for the first time and a laboratory tank filled with hydride/nanocarbon composite was built and tested for the first time. The material was cycled and, after a formation phase, showed stable reversible capacities at around 2 wt.% H. Moreover, it was demonstrated that the reactivity in air can be lowered by nanocoatings based on self-assembled layers of polyelectrolytes and that borohydrides do not emit toxic trace gases such as diborane when infiltrated in a nanocarbon template.

4.1.2 Summary description of project context and objectives

Hydrogen storage is regarded one of the most critical issues, which has to be solved before a technically and economically viable hydrogen economy can be established. As gravimetric energy density of H_2 is extremely high in contrast to its volumetric storage density which is very low, the most important technical and economic challenges to be overcome are the storage density related to the system (including tank, heat management, and valves), the costs of the system, its safety, the refuelling time, and the ability to deliver enough hydrogen during the drain cycle. So far, the technical targets for automotive applications have not been reached by any of the current technologies, be it compressed (CGH2) or liquefied (LH2) hydrogen or storage in a state-of-the art metal hydride. However, while the physical limits of the storage capacity for the physical storage technologies have been more or less reached, there is still potential for improvement by storing hydrogen as a metal hydride.

Hence, it was one of the major goals of the research in this project to develop hydrogen storage materials with high storage densities, appropriate thermodynamic properties and fast kinetics for hydrogen exchange. In that context, the **following issues were addressed by NANOHy**:

Complex hydrides based on Al (alanates), and B (boranates) exhibit very high hydrogen content up to 20 mass% H. Nevertheless, although these materials are highly interesting in principal, the systems still cannot be used in technical applications, due to the following reasons:

1. The **thermodynamic properties** of the pure hydride phases are not appropriate and the materials are mostly too stable. This makes decomposition temperatures of more than 200 °C necessary which is too high if the application is in the technical environment of a PEM fuel cell.
2. The hydrogenation/dehydrogenation **kinetics** is too slow for practical purposes. It has been shown in several cases that the transformation processes are dominated by materials transport kinetics.
3. The **reversibility** during cycling is interfered by the separation of phases which form during the dehydrogenation of the material. These phases may segregate and grow leading to a slow-down of the kinetics and the formation of inert fractions in the sample which cannot be rehydrogenated during cycling.
4. Complex hydrides based on nitrogen and boron may decompose under the **formation of unwanted volatile species** such as ammonia (NH_3) or diborane (B_2H_6) as by-product. These gases are toxic to both fuel cell catalysts and the environment. Moreover, loss of these species during cycling leads to a gradual degradation of the storage material associated with a reduction of the storage capacity.
5. The hydrides may self-ignite when in contact with air which is an issue for **safe handling** of the material and in case of car accidents.
6. Many alternative nanoscale systems, e.g. those fabricated by thin film methods are interesting model systems for classical hydrides but cannot be **produced in bulk amounts** due to the low production rate and/or the high costs.

Following these critical issues the general goal of the NANOHy project was to produce nanocompositic materials for hydrogen storage which have altered properties with respect to working temperature and pressure, an enhanced reversibility, and controlled interaction between the hydride and the environment, leading to improved safety properties. Therefore, a series of technical objectives and targets were derived which are:

- Synthesis of novel complex hydrides with very high hydrogen content (alanates, boranates, amides) as hydrogen carrier materials.

- Synthesis of nanocarbon materials (activated carbons, carbide derived carbons, carbon aerogels, ordered mesoporous carbons, carbon nanofibers) with appropriate surface characteristics for impregnation.
- Synthesis of self-assembled nanofilms (polyanion – polycation pairs) which mediate interactions between colloidal hydride particles and the environment.
- Development of synthesis methods for nanocomposites based on well-defined nanostructured carbon templates and complex hydrides with high hydrogen content.
- Synthesis of nanodispersed and confined complex hydrides with particle sizes < 5nm.
- Synthesis of nanocomposites which are both well-defined model systems for fundamental studies and up-scalable materials for practical applications.
- Characterization of the microstructure of encapsulated hydride nanoparticles.
- Fundamental understanding, quantification and distinction (also based on theoretical calculations) of size and interface effects of hydrides on the nanoscale.
- Synthesis of bulk amounts of nanocomposite material (several 100 g)
- Integration into laboratory tank. Test run and cycling of the system.
- Techno-economical evaluation and exploitation.

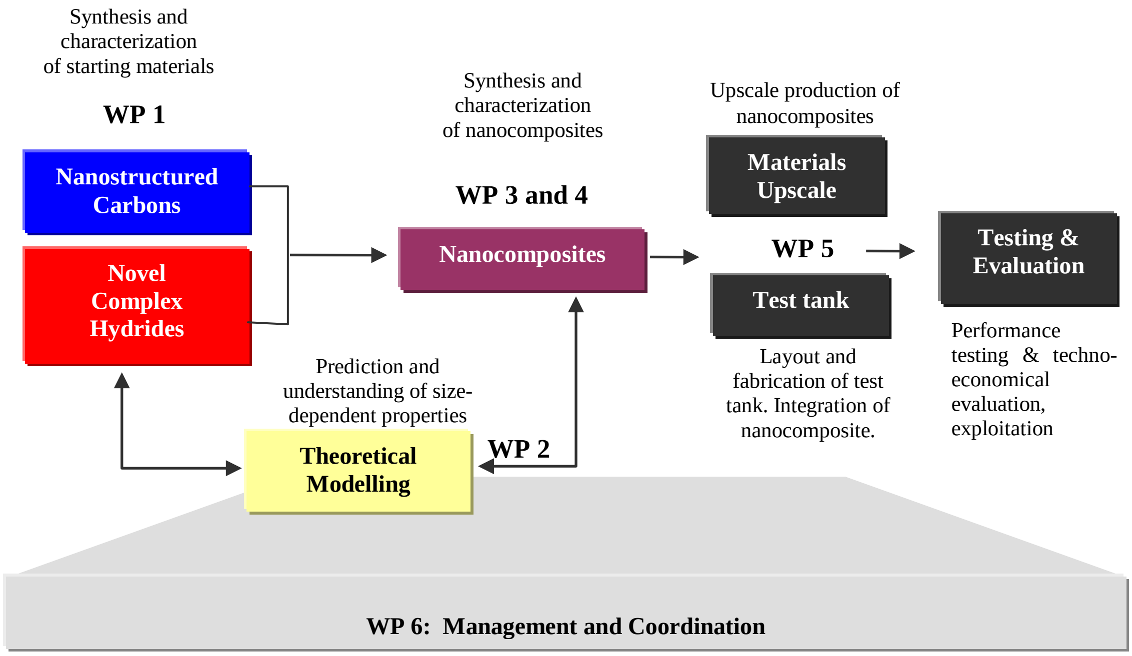
The quantitative technical target parameters of the storage systems developed in NANOHy were considerably beyond those of the current state-of-the art in the field and are summarized in the following table. The improvements are given in absolute numbers or relative to the bulk data of the materials, as indicated.

Table 1: Summary of targets for the nanocomposites developed in NANOHy.

Parameter	***Unit***	***Target***
Particle size of nanodispersed complex hydrides	nm	< 5
Gravimetric density (ref. to materials weight) at 100-200°C	mass% H	> 8
Refuelling rate	g/s	0.5
Desorption temperature of H_2	K	Lowered by > 50 K compared to ball-milled material; targeted temperatures are < 200 °C
Reaction enthalpy ($\Delta H_{reaction}$)	kJ/mol H_2	30-40
Amount of material produced	kg	Batches of 0.5 kg - 1 kg in WP 5.
Reduction of desorbed diborane	%	> 90
Safety	-	No self-ignition in contact with air.
Tank	-	At least 1 laboratory test tank for 0.5-1 kg of material

4.1.3 Main S&T results/foregrounds

The work plan of NANOHy was structured in a straightforward and simple manner, starting from the preparation of building blocks for the nanocomposites in WP 1, over the synthesis of nanocomposites in WP 3, the structural and physical characterization of the nanocomposites in WP 4 up to the upscale and integration of a selected composite into a test tank in WP 5. WP 2 was a modeling activity with cross-cutting tasks which not only predicted the behaviour of freestanding and nanoconfined hydride nanoparticles but was also in close contact with the experimental groups in order to verify in- and output of the models thus leading to an improvement of the model approach and of the accuracy of the predictions.



4.1.4 Work package 1: Synthesis and characterization of H carrier materials and nanostructured carbon scaffolds

Objectives of the planned investigations of the work package

The main objectives of WP 1 were to provide the starting materials for the preparation of the nanocomposites which are the targeted systems of the project. Complex hydrides with high hydrogen contents were prepared as hydrogen carriers, while several types of nanostructured carbon materials were generated as scaffolds for the nanocomposites that were developed in WP3.

The partners discussed and agreed upon a list of complex hydrides, according to the state-of-the art. All these hydrides had high hydrogen content and were applicable for the purpose of the project. The following **hydrides** were chosen as active materials:

> Magnesium borohydride ($Mg(BH_4)_2$), calcium borohydride ($Ca(BH_4)_2$), aluminium hydride (AlH_3), lithium borohydride ($LiBH_4$), sodium borohydride ($NaBH_4$), magnesium hydride (MgH_2)

As **templates**, the following nanocarbon materials were chosen:

> Microporous carbons (Activated Carbons-ACs), mesoporous carbons (Carbon Aerogels-CAs and ordered mesoporous carbons-OMCs), and carbon nano fibers (CNFs).

Synthesis and characterization of the starting materials

The two classes of starting materials were synthesized, characterized and shared among the partners: **Nanocarbon materials** which serve as scaffolds and **complex hydrides** which shall be impregnated into the scaffolds in order to form nanocomposites. In a second approach the complex hydrides served as base materials for coating them with self-assembled layers of polyelectrolytes.

It was demonstrated that the **synthesis procedures** demonstrably work for both the complex hydrides and the nanocarbons which were produced by several partners in the project. In total, several 100 g of carbon templates and approximately 100 g of complex hydrides were produced. In addition, KIT demonstrated that it is possible to synthesize single batches of 20 g nanoporous carbon and batches of 10 g $Mg(BH_4)_2$.

The **complex hydrides** which were synthesized were characterized in order to check for the purity, the phases produced, structural and thermal properties. The phase composition of the novel hydrides was analysed by powder X-ray diffraction, XRD, also at the synchrotron. The H-content and amount of potential impurities of C and N was analysed by elemental analysis, while impurities with short-range order were characterized by infrared spectroscopy, FTIR. Thermal analysis methods such as thermo gravimetric analysis (TGA) and Differential Scanning calorimetry (DSC) with or without coupling to a mass spectrometer (MS) were used to detect phase transformation and hydrogen desorption and absorption behaviour. Incoherent inelastic neutron spectroscopy was used as a reliable method for the investigation of the hydrogen dynamics in metal hydrides, and as a validation tool for lattice dynamics simulations of the materials. These features also helped as an effective input and comparison for the modelling activity in WP 2.

The decomposition enthalpies of the complex hydrides were determined by high-pressure DSC under H_2 atmosphere. The bulk data was exchanged with WP 2 and used there as input, but also for comparison with the theoretical calculations.

Thus, a **data base was built** in order to be able to compare the properties of the nanocomposites produced in WP 3 and characterized in WP 4 with the properties of the bulk materials.

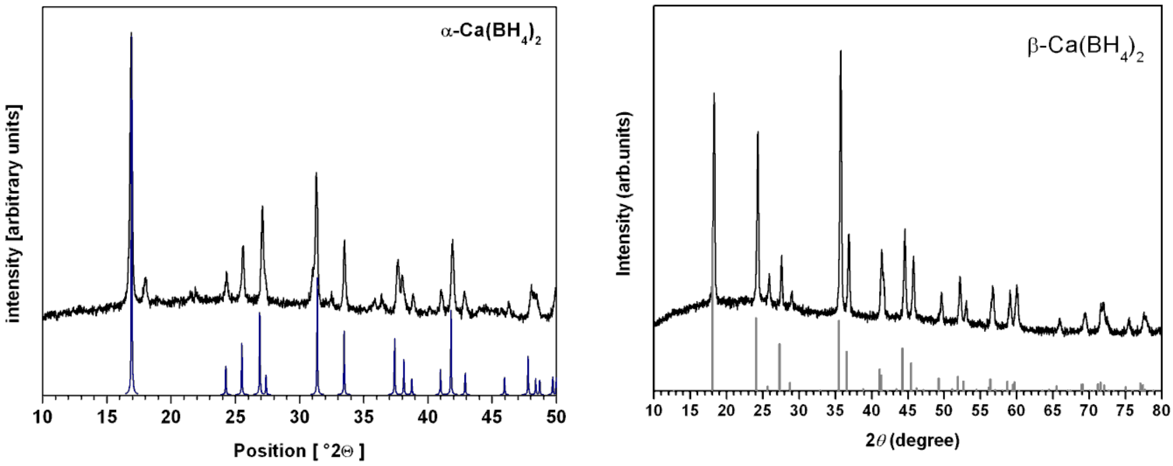


Figure 1: Measured powder X ray pattern (top) of $Ca(BH_4)_2$ *and calculated pattern (bottom), for alpha phase (left diagram) and beta phase (right diagram). The alpha phase contains a small impurity of the beta phase.*

Various methods were used to **study the morphology, the porous structure and vibrational properties of the nanocarbons** which were produced as support for the later infiltration with complex hydrides. The methods included physisorption method, Small Angle Neutron Scattering (SANS), Raman scattering, and electron microscopy (HR-TEM, SEM). A data set was obtained which served as a basis for the nanocomposite synthesis and comparison with the data of the infiltrated nanocarbons.

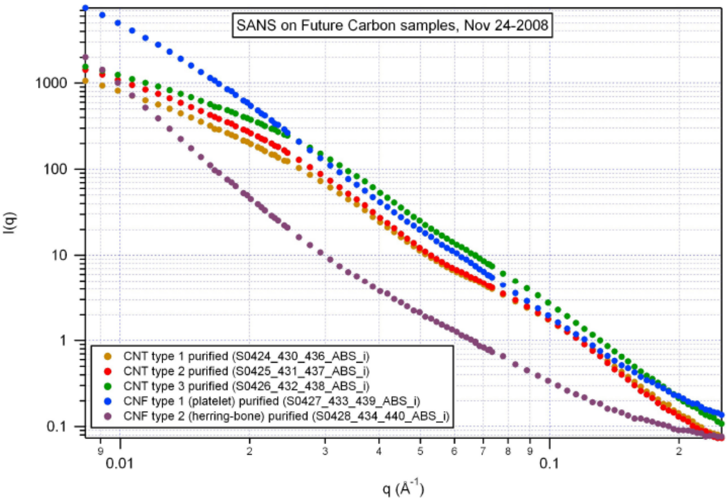


Figure 2: SANS data of five different nanocarbon types produced by Future Carbon GmbH.

Whereas BET analysis was used as a standard tool for quality control, determinantion of specific surface areas and differential pore volumina, SANS is a unique tool which could be used to unequivocably identify whether material was infiltrated in the pores or not (see also WP 3).

4.1.5 Work package 2: Modelling

Objectives of the planned investigations of the work package

WP 2 aimed at the use of advanced computational approaches for modelling the thermodynamic size and interface effects on the developed hydrides. Moreover, new phases with high hydrogen content should be calculated and evaluated. The influence of the particle size for optimised thermodynamic properties in selected hydrides should be predicted, and compared to experimental results which were obtained in WP 1, 3, and 4.

Modelling of size and interface effects

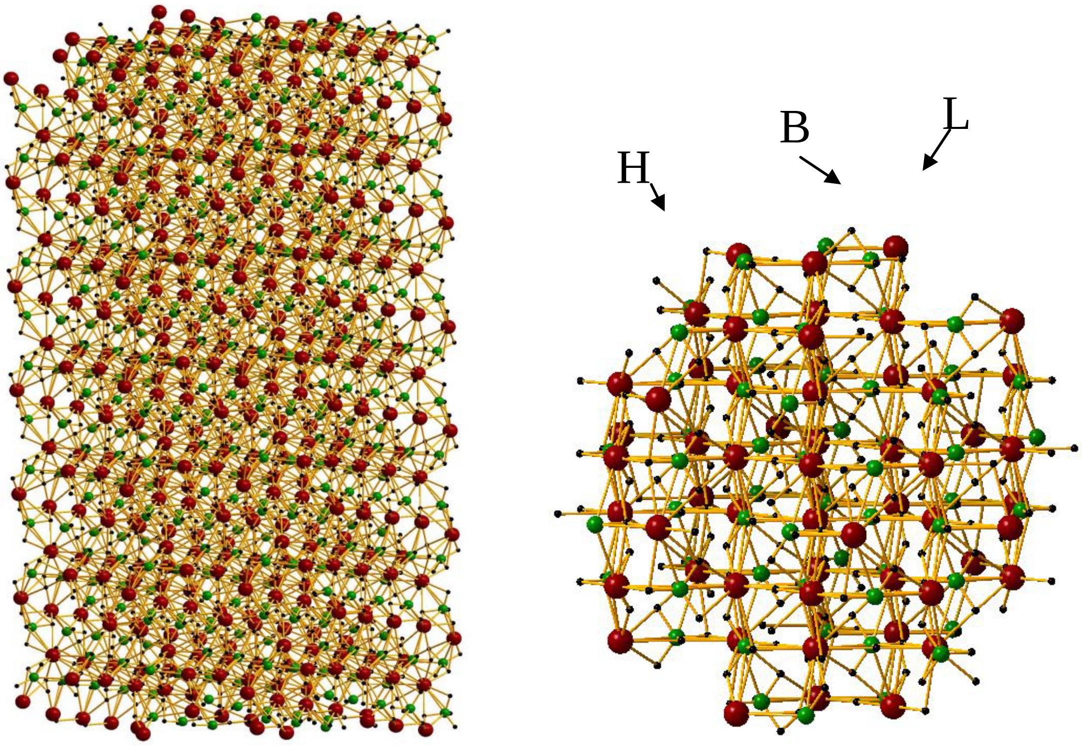
From the charge density, charge transfer, electron localization function, density of states, crystal orbital Hamilton population, and Mulliken as well as Born effective charge analyses, the chemical bonding behaviour of constituents of nanophases at the surface and inside the material was evaluated and its deviation with respect to bulk materials was investigated. From the calculated total energy, the surface energy was calculated as a function of particle size and shape. The surface energy of a crystal was calculated using the following equation

$$E_{surf}(n) = [E_{tot}(n) - E_{bulk}(n)]/2A$$

The calculations performed aimed at **modeling complex hydride clusters** and **nanowhiskers**, free standing or **embedded in a carbonaceous matrix**. The calculations yielded critical sizes of complex hydride nanoparticles below which substantial destabilization and, hence, lower working temperature can be expected.

The calculations predicted that the **particle size** of various hydrides should be lower than 2 nm in order to observe this desirable effect. The bond energies for hydrogen atoms at the surface of such particles are considerably decreased in such a case and the total energy increases drastically of the system. If the cluster size and nano-whisker diameter is further reduced, the relative energy of the clusters/nano-whiskers drastically changes, which indicates strong destabilization of small particles. This also suggests that the thermodynamic properties and in particular the hydrogen sorption temperature is expected to reduce in nanophases compared with that in bulk materials. This predicts that the decomposition temperature can be reduced which is desired for the utilization of complex hydrides for energy storage applications. Further, the surface-to-volume ratio increases upon decreasing the cluster/nanowhisker size. Since the surface atoms have a lower coordination, the average number of bonds is lower for smaller clusters.

These results gave an important advice for the experimental groups which are working on the synthesis of nanocomposites based on complex hydrides.



(a) (b)

Figure 3: Optimized stable (a) nano-whiskers and (b) nanocluster of $LiBH_4$ derived from α-$LiBH_4$ structure.

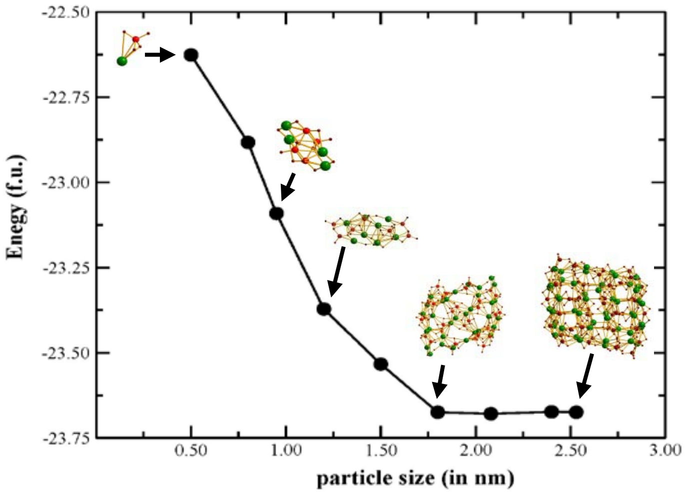


Figure 4: Calculated total energy (in eV/f.u.) as a function of $LiBH_4$ cluster size (in nm).

Table 2: The calculated surface energies for selected compounds are listed in the Table.

Direction	$NaBH_4$	KBH_4	$Mg(AlH_4)_2$	$Ca(BH_4)_2$
(001)	1.89	1.64	2.67	0.23
(010)	1.36	1.29	1.56	0.26
(011)	0.24	0.30	1.07	0.19
(100)	1.36	1.29	1.56	0.21
(101)	0.24	0.31	2.00	1.76
(110)	1.75	1.67	0.83	0.21
(111)	0.82	0.73	0.94	0.23

Further studies investigated the properties of hydrides when **infiltrated in a nanoporous carbon**. MgH_2 was one of the compounds which were studied in different model cases:

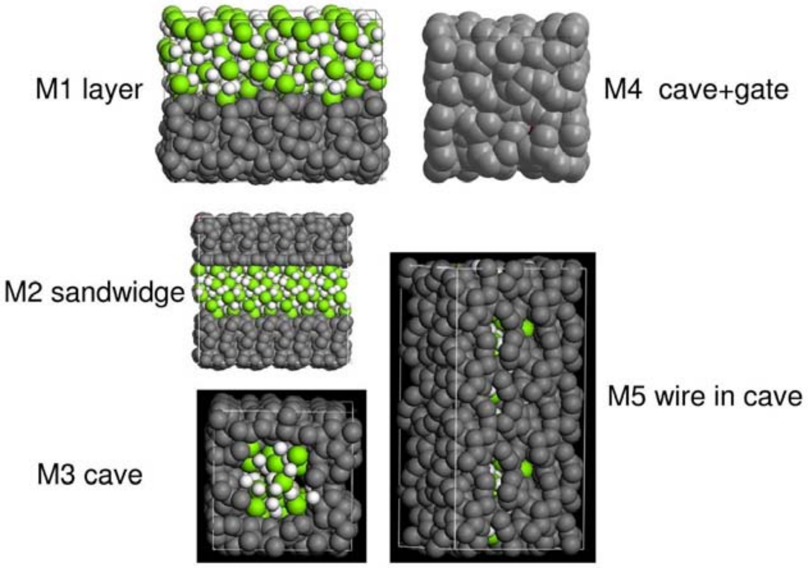


Figure 5: Considered structure models in this study; M1: Over layers of MgH_2 in amorphous carbon (AC) substrate; M2: AC-MgH_2-AC(sandwich /multilayer) model;, M3: MgH_2 in the carbon scaffold; M4: MgH_2 nano dot is placed in the closed scaffolds and M5: MgH_2 nano wire in the carbon scaffolds.

The results clearly indicated a **strong influence of the hydride-wall interaction** leading to a broadening of the distribution of states. In all these structure models, the calculated Mg-H distances versus number of bonds for the biggest clusters/whiskers indicate that the values were scattered compared with that in the corresponding bulk phase. Especially most of the Mg-H bonds have **longer bond distances** than that in the bulk. It should be noted that in all these structure models the initial $LiBH_4$ and MgH_2 **structures were completely rearranged**. This type of structural arrangement is expected in nano- and amorphous-phases with no three dimensional crystallinity owing to reduction in coordination number of atoms.

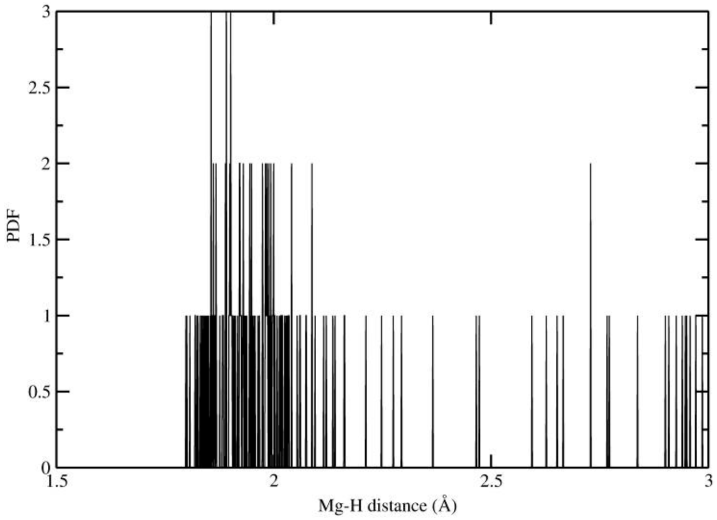


Figure 6: Calculated inter-atomic distances between Mg-H in the optimized M2 model. The corresponding Mg-H distance in the bulk phase is 1.95Å.

In all the structure models which were investigated, the calculated Mg-H distances versus number of bonds for the biggest clusters/whiskers indicate that the values were scattered compared with that in the corresponding bulk phase. Especially most of the Mg-H bonds have longer bond distances than that in the bulk. It should be noted that the initial MgH_2 structure is completely rearranged in all of the models. This type of structural arrangement is expected in nano- and amorphous-phases with no three dimensional crystallinity owing to a reduction in the coordination number of atoms.

A **comparison with experimental data**, especially the nanoconfined MgH_2 proved the correctness and accuracy of these modeling results. A thermodynamic destabilization was found which was similar to the numbers predicted in this study (see also WP 4).

Prediction of new complex hydride phases with high H-content

The **crystal structure, electronic structure, and thermodynamic properties** of the $M\text{CaH}_3$ (M = Li, Na, K, Rb, Cs) series were studied by state-of-the-art density-functional calculations. For the experimentally known $RbCaH_3$ and $CsCaH_3$ phases, the ground-state structure was successfully reproduced within the accuracy of the density-functional approach. The ground-state crystal structures for $M\text{CaH}_3$ (M = Li, Na, K) phases were predicted from structural optimization of a number of structures using force as well as stress minimizations. The predicted crystal structures for $LiCaH_3$ and $NaCaH_3$ were found to have rhombohedral and tri-clinic structures respectively, with insulating behaviour. $KCaH_3$ stabilizes in orthorhombic structure whereas $RbCaH_3$ and $KCaH_3$ stabilize in cubic structures. Formation energies for the $M\text{CaH}_3$ series were calculated for different possible reaction pathways. The phonon density of states for the lattices was calculated by using a direct force constant method and it shows that all the predicted phases are dynamically stable.

The ground state structure of the CaB_2H_2 phase was predicted to be in tetragonal structure [space group P-3 m1 (no. 161)]. From our lattice dynamic simulation we found that this phase is dynamically stable and we also simulated Raman spectra for this phase.

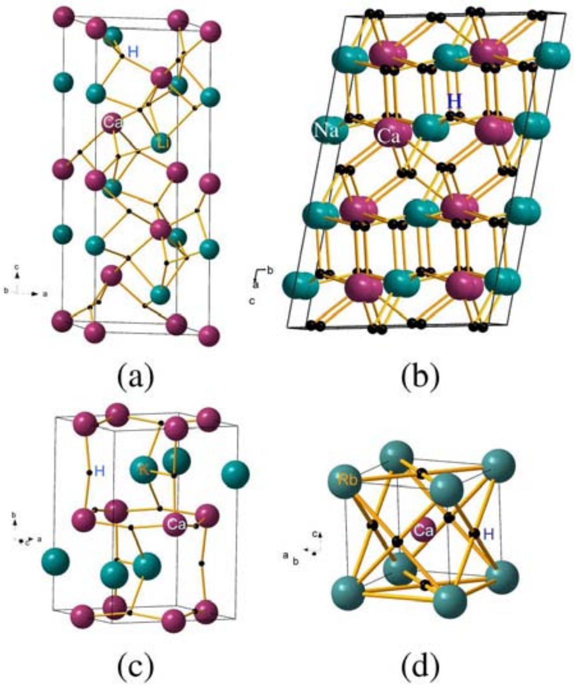


Figure 7: Theoretically predicted crystal structures for $LiCaH_3$, (b) $NaCaH_3$, (c) $KCaH_3$, (d) $RbCaH_3$, and $CsCaH_3$

All $M\text{CaH}_3$ compounds were seen to exhibit **high formation energies**. For all the studied phases, synthesis from the elements is energetically more favourable than other paths and we suggest that it should be possible to synthesize/stabilize these compounds using CaH_2 and M by offering H_2 under pressure or H_2 flow.

Table 3: Calculated hydride formation energy (∆H; in kJ/mol) for the $MCaH_3$ series.

Compound	∆H1	∆H2	∆H3	∆H4
$LiCaH_3$	17.74	-70.01	-273.25	-149.51
$NaCaH_3$	34.45	-10.55	-177.79	-132.79
$KCaH_3$	17.03	-25.62	-192.86	-150.21
$RbCaH_3$	10.32	-24.67	-191.91	-156.93
$CsCaH_3$	12.84	-24.26	-191.50	-154.4

4.1.6 Work package 3: Preparation of nanocomposites

Objectives of the planned investigations of the work package

Before the work of NANOHy, complex hydrides with high hydrogen content were mostly prepared by mixing them with dopants and ball-milling which has not been suitable to alter the thermodynamic properties and/or sufficiently increase the kinetics so that the working temperatures and pressures could be lowered to technically viable values. Moreover, other problems were observed such as the co-emission of volatile by-products with hydrogen and the high reactivity in air. NANOHy aimed at advancing significantly the state-of-the-art in the area of light/complex hydrides. This should be done by preparation of hydride nanoparticles with altered thermodynamic and kinetic properties which are encapsulated in a matrix in order to mediate the interaction with the environment and to prevent the systems from particle growth. It was the purpose of this project to use only complex hydrides with high hydrogen content because due to their inertness, the carbon or polymer matrix leads to losses of the overall storage capacity which can be accepted if the storage capacity of the hydride is high enough and the preparation process leads to optimal dispersion of the hydride.

The key challenge in WP 3 was to synthesize the target materials in the project from the starting materials which were produced in WP 1. Nanocompositic hydrides systems consisting of confined nanoparticles with sizes in the lower nanometre range were to be synthesized by melt impregnation and wet incipient impregnation of nanostructured carbon templates with complex hydrides and by self-assembled coating of colloidal hydride particles.

Infiltration of carbons

One of most critical issues and the biggest scientific/technical risk was the question whether or not hydrides can successfully be infiltrated into micropores. This is mostly due to their size < 2 nm and potential problems in the wettability of the pores. Hence, the work in WP 3 of NANOHy focused the **development of infiltration methods and the characterization of the degree of infiltration**.

A major focus of the activities was therefore the development of melt infiltration methods and wet incipient impregnation of hydrides into nanocarbons. New methods had to be developed to successfully infiltrate the hydrides into the micropores. The **synthesis and characterization of nanocomposites** was extended by varying the carbon supports for infiltrated $NaAlH_4$ and $Mg(BH_4)_2$ in order to study the influence of pore structures and to exclude the influence of metal impurities in the natural activated carbon.

After synthesis and careful investigation of the numerous nanocarbons which were on the initial list the following types were chosen as templates:

AC1	Carbon powder, activated (Alfa Aesar)
AC2	Carbon, activated, _4+8 mesh (Alfa Aesar)
PFA600	non-commercial carbon, synthesized at FZK
ACF-25	activated carbon fibers (Kynol)
IRH-33	activated carbon provided by UQTR

A new method was developed for the infiltration of $Mg(BH_4)_2$, MgH_2, and AlH_3. The method includes a cryogenic step and allows almost complete filling of the pores. Thermal properties and H sorption behaviour of the nanocomposites were investigated. Using this method, powder X-ray diffraction patterns for $Mg(BH_4)_2$/AC1 composites with lower $Mg(BH_4)_2$ loadings (sample $Mg(BH_4)_2$/AC1(0.15) and $Mg(BH_4)_2$/AC1(0.25)) show no or just a few broad reflection peaks, which indicates the confinement of hydride to the nano scale of the carbon scaffold, see Figure below. In order to increase the hydrogen desorption capacity, a composite with a higher hydride loading (44 wt %) has been prepared (sample $Mg(BH_4)_2$/AC1(0.44)), which presents sharper XRD reflections and therefore suggests that $Mg(BH_4)_2$ partly remains as bulk phase on the surface of carbon template.

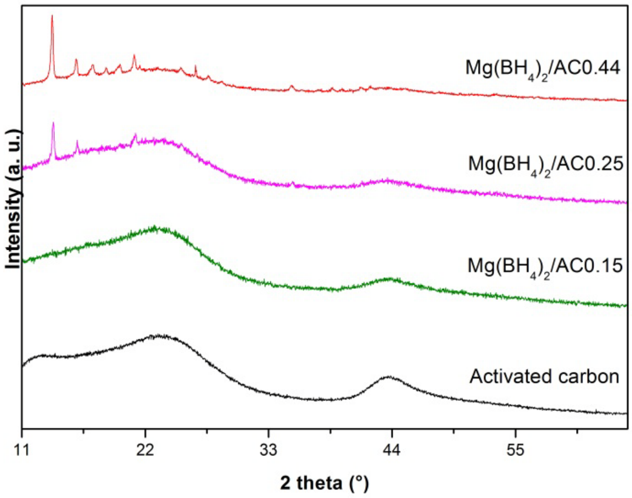


Figure 8: Powder X-ray diffraction patterns of $Mg(BH_4)_2$/AC1 nanocomposites.

Another group of composite materials that have been synthesized and characterized was based on **sodium aluminumtetrahydride ($NaAlH_4$)**. The hydride decomposes according to

$$3\ NaAlH_4 \rightarrow Na_3AlH_6 + 2\ Al + 3\ H_2 \rightarrow 3\ NaH + 3\ Al + 4.5\ H_2$$

The infiltration was carried out by melting procedures, i.e. a powder mixture of $NaAlH_4$ and activated carbon (AC) was heated for 2 hours in a stainless steel reactor at 190°C (T_m = 181°C) under a 140 bar H_2 pressure in order to prevent decomposition of the hydride. Thus, about 3 g composite material was produced per batch.

Physisorption analysis clearly showed a strong **decrease of the open pore volume** from of 1170 $m^2\ g^{-1}$ for pure AC2 vs. 60 $m^2\ g^{-1}$ for the infiltrated composite, representing a decrease of 95 %. The microporosity was retained in the composite, but while the pure carbon powder revealed a large total pore volume of 0.48 $cm^3\ g^{-1}$ and no mesoporosity at all, the total pore volume of 0.04 $cm^3\ g^{-1}$ found for the composite material was more than one order of magnitude smaller. The pore size distribution shows a shift towards larger pore diameters with a significant contribution of pores in the mesoporous range. Such a decrease in surface area as well as porosity is in accordance with the incorporation of a significant amount of SAH into the pores of the carbon scaffold.

While the **pores seemed to be almost completely filled**, the X-ray diffraction data of the resulting composites $NaAlH_4$/AC1 and $NaAlH_4$/PFA600 revealed a partly decomposition of the alanate in the course of the melting procedure. In case of $NaAlH_4$/PFA600, Al appeared to be the only well-defined phase, the remaining features of the XRD are broad signals caused by the highly amorphous carbon scaffold and very weak $NaAlH_4$ signals. The XRD of the second composite, $NaAlH_4$/AC1, clearly showed well-defined $NaAlH_4$ peaks, but, as in case of $NaAlH_4$/PFA600, also revealed the presence of an Al phase formed upon partly decomposition during the melting process.

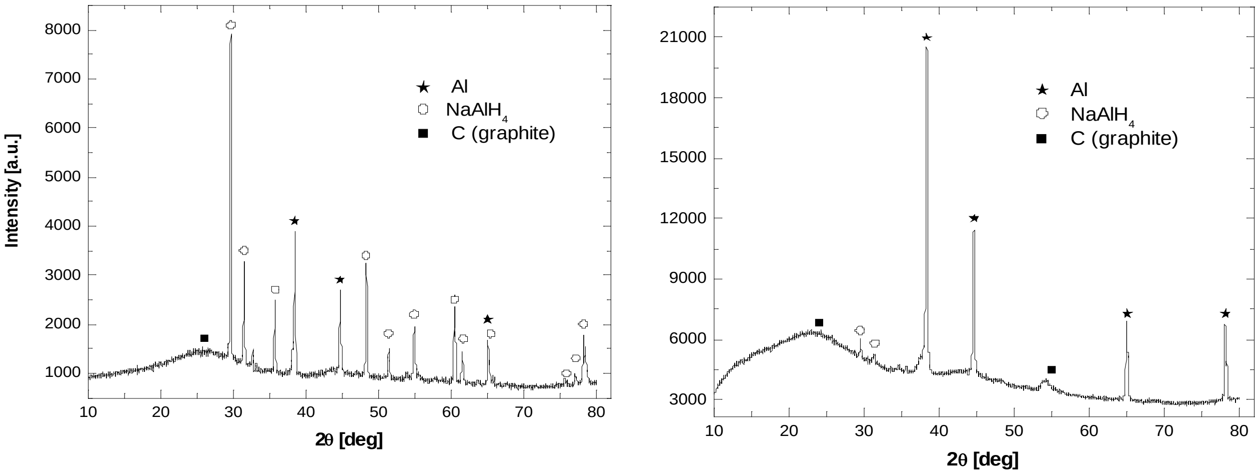


Figure 9: X-ray diffraction patterns of composites $NaAlH_4$/AC2 (left) and $NaAlH_4$/PFA600 (right).

Magnesium hydride (MgH_2) based composites were prepared by **wet-chemical infiltration** with a heptane solution of the organometallic precursor Bu_2Mg. After the impregnation, the precursor was thermally decomposed at 230 °C under 60 bar hydrogen pressure and thus directly hydrogenated, yielding the MgH_2 composites.

$$Bu_2Mg/\text{carbon} \xrightarrow[230\ ^\circ\text{C}]{60\ \text{bar}\ H_2} MgH_2/\text{carbon} + \text{butane} \qquad (1)$$

The occurrence of exothermal hydrogenation of Bu_2Mg was monitored in DSC experiments by heating up the Bu_2Mg/ACF composite to 230 °C under hydrogen pressure. In order to prevent any evaporation of Bu_2Mg out of the carbon scaffold, 60 bar of H_2 was applied in an autoclave type of reactor. X-ray diffraction profile of MgH_2/carbon composites revealed broadened diffraction patterns of MgH_2, which indicated a nanoscale grain size of MgH_2 incorporated in the carbon scaffold. After the incorporation of MgH_2 in ACF-25, the surface area of the composite was and the pore volume of the micropore (< 3 nm) was reduced to 1100 m^2/g and 0.40 cm^3/g, respectively, which indicated the accomplishment of the infiltration of MgH_2 in the micropores of the carbon scaffold. A further analysis by SANS confirmed the nanoscale dispersion of the hydride in the carbon, see WP 4.

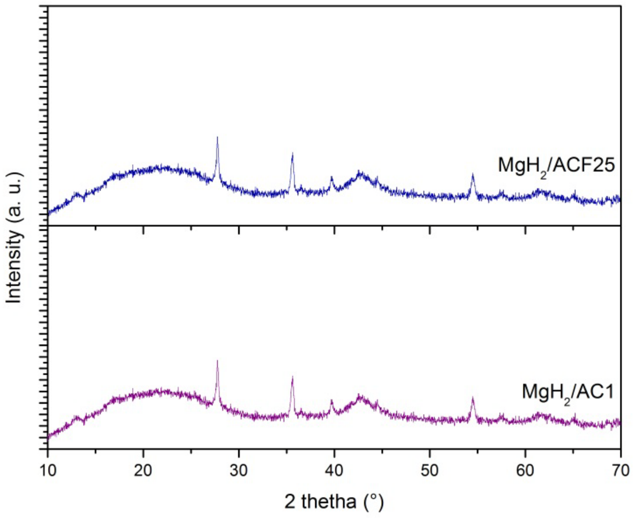


Figure 10: Powder X-ray diffraction patterns of MgH_2/nanocarbons.

A further type of system was low melting **eutectic mixtures of different borohydrides**. It was recently reported that in the mixed system of $LiBH_4$ (LBH) and $Ca(BH_4)_2$ (CBH), the ratio 0.7LBH / 0.3CBH represents an eutectic composition with a melting point of 200 °C, compared to the melting point of 280 °C of pure LBH (CBH decomposes at 360 °C without prior melting). This low melting composite showed a decreased decomposition temperature relative to its pure components and can at least partly be rehydrogenated (in presence of a catalyst).

Therefore, we prepared a composite of 0.7 LBH / 0.3 CBH and the activated carbon AC2. The powder XRD of the infiltrated material only showed one weak signal that might originate from LiH. The DSC trace of the pure 0.7LBH / 0.3CBH mixture was in good agreement with literature data, i.e. phase transitions at 110 °C and 150°C, the eutectic melting at 200 °C and the decomposition starting from 340 °C. On the other hand, the DSC trace of the melt infiltrated composite showed only a weak endothermic signal centered around 310 °C, but no phase transition or melting can be observed. This indicates decomposition of the material which could be avoided when a hydrogen backpressure of 100 bar was used during the melt impregnation.

The $LiBH_4Mg(BH_4)_2$/IRH33 and its related isotopic nanocomposites have been also prepared by melt infiltration method. As a representative example, 0.5 g of activated carbon IRH33 was mixed with 0.187 g of $LiBH_4Mg(BH_4)_2$ and heated at 180 °C under 30 bar of H_2 for 1 hour.

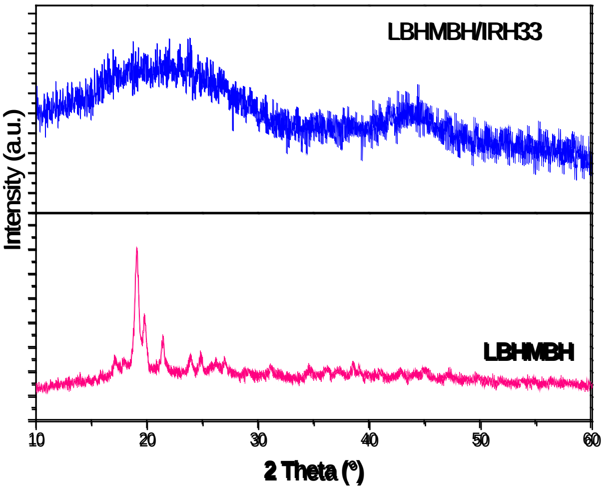


Figure 11: X-ray diffraction patterns of the as-prepared $LiBH_4+Mg(BH_4)_2$/IRH33 nanocomposite.

Nanocoated hydride colloids

The focus of the experimental activities in this task was on synthesis and investigation of nanocomposites which were prepared by coating hydride nanoparticles with **self-assembled polyelectrolyte layers** and covering their surface with **polymer nanofilm**. The polymer shell has to be water impermeable but hydrogen permeable and provide reversible absorption/desorption of hydrogen. Two different methods of coating were examined, the Layer-by-Layer self-assembly of opposite charged polyelectrolytes and the coating with a polystyrene (PS) shell by co-precipitation.

Sodium borohydride particles were encapsulated within polymer films by the Layer-by-Layer self-assembly of opposite charged polyelectrolytes (polyethyleneimine (PEI) and polyacrylonitrile-co-butadiene-co-acrylic acid (PABA)). The polymer nanofilms fabrication was performed using dichloromethane as a working media. The IR-spectroscopy was applied to investigate the chemical interaction between the polyelectrolytes. The multilayer film preparation was verified by Z-potential measurements, scanning electron microscopy and confocal laser microscopy. The **stability of sodium borohydride protected with the polyelectrolyte shell was increased** compared to the pure material in 12 times at the outdoor conditions.

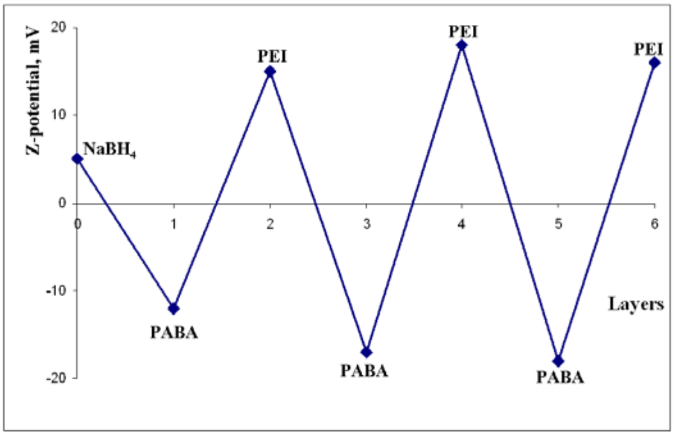


Figure 12: Z-potential as a function of layers number of sodium borohydride particles coated with poly(acrylo-nitrile-co-butadiene-co-acrylic acid(PABA)) and polyethyleneimine (PEI).

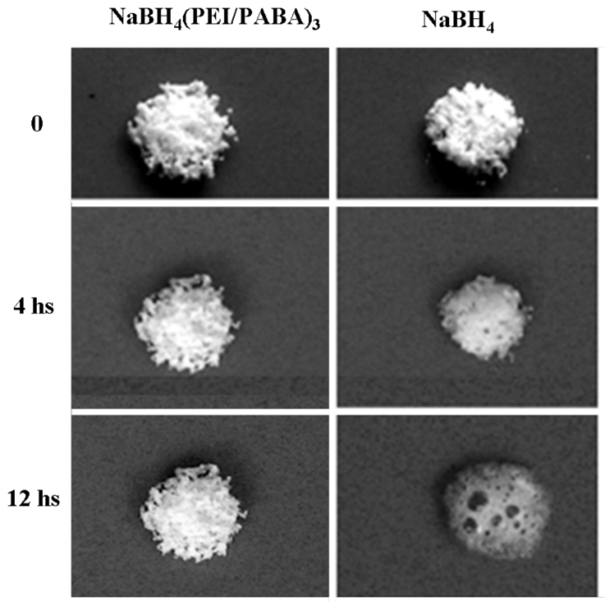


Figure 13: Photographs of the protected and pure sodium borohydride during the storing process. The samples were put on the glass surface and kept in the open. The images were taken by the optical photo camera..

Another simple approach for the protection of hydrogen storage materials is based on **interfacial polymer precipitation** induced by solvent evaporation. Sodium borohydride (SBH) was **successfully protected with a polystyrene (PS) shell** by co-precipitation. This shell provides a hydrophobic barrier for water diffusion into the container interior. Simultaneous nucleation of SBH inside the droplets of the disperse phase and formation of a PS shell around during gradual solvent evaporation lead to the development of the structures consisting of a SBH core and the polymer shell. Confocal fluorescence microscopy (CLSM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed a crystalline interior and a polymer shell of the fabricated microcontainers. FTIR spectroscopy proves the presence of a SBH core and a PS shell. The stability of SBH microcontainers is increased as compared to the unprotected material by 2.5 times during storage at 100 % humidity.

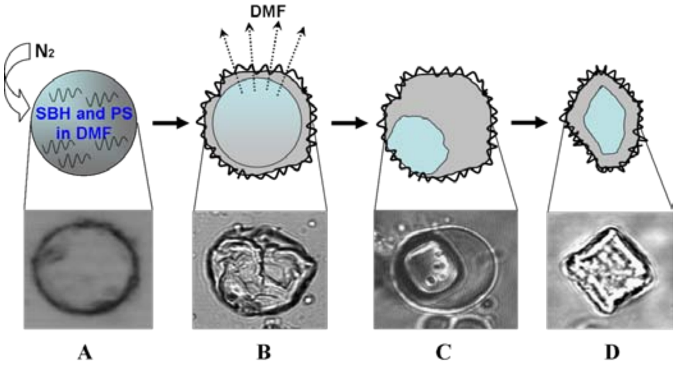


Figure 14: Gradual formation of the core-shell structure of hydrogen-enriched materials upon solvent evaporation.

4.1.7 Work package 4: Characterization of nanocomposites

Objectives of the planned investigations of the work package

Work package 4 dealt with the assessment of fundamental properties (microstructure of the nanoscale hydride systems, thermodynamic and kinetic properties of the nanocomposites) of the materials that were produced in WP 3. In addition, the amount of volatile by-products was analysed through desorption experiments and the thermal conductivity and safety-relevant properties were determined. The results served also as feedback for the synthesis (WP1) and the modelling (WP2) work in order to improve both the preparation processes and the theoretical models.

Structural characterization

The results in the following are only a selection of the broad structural investigations on a series of hydrides infiltrated in microporous and mesoporous carbon templates. The presentation has been focused on systems in microporous scaffolds which have the potential to exhibit both kinetic and thermodynamic effects and which were investigated by the NANOHy consortium for the first time.

A breakthrough was achieved in the characterization of nanoconfined hydrides in WP 4. In order to check whether hydride material has been successfully infiltrated in a porous scaffold, HR-TEM has been tried by several groups, also within NANOHy, but the materials are highly sensitive to the electron beam and therefore cannot be studied at high magnification. Instead, investigation methods such as X ray powder diffraction, and physisorption method have been applied which either indicate that there are no large crystallites with a long range order present in the sample or that the pore volume has been reduced by the infiltration procedure.

Hence, these are no methods which would be capable of **detecting very small nanoparticles (< 3 nm) in the material directly**. This was only achieved in a joint effort of several partners in NANOHy where an **isotope labeled complex hydride**, $Mg(^{11}BD_4)_2$, was prepared, infiltrated in microporous activated carbon, and investigated by Small-Angle Neutron Scattering (SANS). Thus, it was possible for the first time to **directly proof that the preparation procedures lead to nanoconfined hydride particles with a characteristic size in the order of 2-3 nm.** The data also indicated a smoothening of the surface of the nanocarbon, due to the pores which are filled by the hydride. The findings are of particular importance for the scientific community because there has been a debate if the infiltration process at all leads to a hydride system which is dispersed on the lower nanometer scale.

Detailed inspection of the $M^{11}BD$/AC1 curve (see Figure 15) shows that there is a cut-off in the pattern around $q = 0.025$ Å^{-1}. Below this value the infiltrated $M^{11}BD$ and the AC1 curves behave similarly (near parallel curves), whereas above this point there is a slope change for the Mg-borodeuterate curve, (slope drops from -2.6 to -2.9). The q-value for this cut-off represents a characteristic dimension in the system, here $d \sim 1/q = 4$ nm, where the $M^{11}BD$ particles in the system scatter differently than the scaffold itself (AC1). Note that this value is close to that obtained by visual inspection of the Figure with indication that the main contribution to the Mg-borodeuterate signal was from particles below ca. 5 nm. Evidently also some larger particles were present, but it is known from PXD measurements that this could only be to a small amount since they do not contribute sufficiently to give detectable diffraction peaks.

The two curves in the Figure are seen to approach each other in the upper q-range, due to the fact that the slope for the Mg-borohydride data is higher here than for the AC1 scaffold itself. This is a sign that the density of the system in the nm-range has become significantly increased after infiltration with Mg-borohydride: The slope α of -2.9 ($I \sim q^{-\alpha}$) found for the borohydride-loaded system in the q-range above $q=0.025$ Å^{-1} corresponds to a mass fractal dimension D_m close to the maximum attainable, i.e. $D_m = 3.0$. The scaffold alone shows a lower slope, $\alpha = -2.6$, characteristic of a considerably more open system, as expected for porous activated carbon. Thus the absorption of Mg-borohydride is seen to significantly reduce the porosity of the scaffold, an observation that would be in accord with a situation where the infiltrated borohydride consists of nm-sized particles that provide a near complete filling of the smallest pores available in this scaffold. Considerable kinetic effects were observed with this nanocomposite.

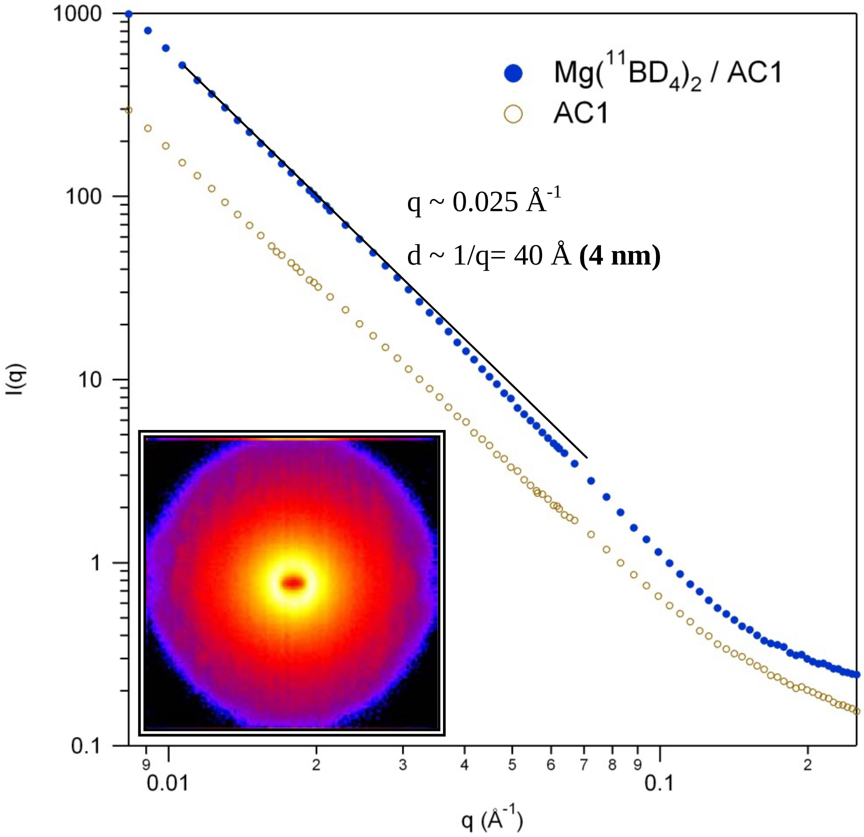


Figure 15: Reduced SANS data for the M^{11}BD$_4$/AC1 compared with the data from the scaffold alone. The straight lines follow the different power law behavior below and above the cut-off point around q = 0.025 Å^{-1}.

Similar experiments were performed with **other nanoconfined materials**, NaAlD$_4$/ACF for example. Also here, SANS **confirmed the small sizes (< 4 nm)** which the NaAlD$_4$ particles have when they are integrated into the scaffold. Accompanying studies with Small Angle X Ray Scattering (SAXS) confirmed the results obtained by SANS. With these nanocomposites both kinetic and thermodynamic effects were observed.

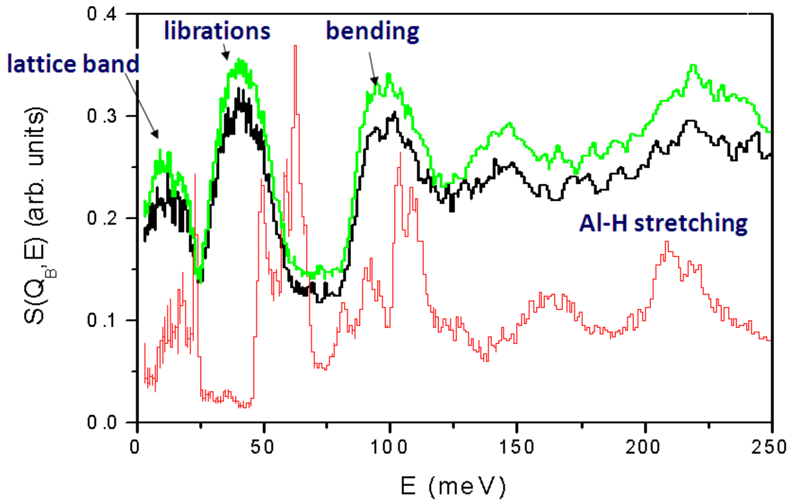


Figure 16: Hydrogen component of the self inelastic structure factor from NaAlH$_4$ /ACF composite as prepared (middle), desorbed and reabsorbed composite (upper) and bulk NaAlH$_4$ (lower), all recorded in backscattering at low temperature. The spectra have been shifted for graphic reasons.

An important scientific result is that the consortium was **able to explain the unusual thermodynamic behavior of complex hydrides** which are infiltrated in microporous carbon scaffolds. Inelastic neutron scattering (INS) was used to elucidate the vibrational properties of nanodispersed NaAlH$_4$ and a general broadening of the states was found, together with a lack of the intermediate Na_3AlH_6. The compound normally appears as a well-defined intermediate stage in hydrogenation/dehydrogenation experiments with catalyzed bulk material. This actually explains the unusual slope of the pressure composition isotherm which does not exhibit any stages but is rather a straight line between the initial state and the final state

Moreover, a **blue shift of the stretching vibrations** was found which leads to a thermodynamic stabilization of the material. An explanation for this effect was given and published. At the same time, a red shift of the librational and bending modes was found which can be explained by a "softening" of the structure when the hydride is in contact with the carbon wall. This effect leads to improved kinetics which was also **observed experimentally and explained and predicted by the modeling group** which has so far been unique in this research field. A substantial agreement between neutron and Raman measurements has been found for the pristine melt-infiltrated sample. However, for the cycled sample, while the neutron experiment shows no appreciable difference with respect to the as-prepared sample, the Raman experiment does not evidence any structure related to $NaAlH_4$, but only a weak feature attributable to Na_3AlH_6. This suggests that the external surface of the hydride nano-particles in close contact with the carbon scaffold may contain Na_3AlH_6 and metallic aluminum clusters, which, differently from the rest of the sample, cannot be easily re-hydrogenated.

Small-angle neutron scattering performed on mixed hydride systems showed that while the bulk **$Li^{11}BD_4$-$Mg(^{11}BD_4)_2$** shows relevant changes during the desorption, the nano-confined material displays no relevant changes at the same conditions. This was confirmed by the indirect Fourier transform performed on the $Li^{11}BD_4$-$Mg(^{11}BD_4)_2$/IRH33 composite before and after heat treatment. The decomposition and release of hydrogen in the composite seems to affect mainly the surface of the particles (which becomes more rough). The mass fractal value also indicated that the nano-composite system became slightly more compact after heat treatment.

A deuterated sample of **nanoconfined MgH_2** was used to measure the particle size of the nanoconfined MgD_2. As shown in Figure 17, SANS measurements indicated that the MgD_2 particles were very small when inside the scaffold, with an average size of around 1 nm. This unusually small particle size can be understood if one considers the particular synthesis procedure which is based on an *in-situ* hydrogenation of a spacious dibutyl-Mg precursor. The reason for the small size is probably the shrinkage which occurs when the spacious butyl groups are replaced by two hydrogen atoms leading to a partial filling of a pore only. The density of Bu_2Mg and MgH_2 is 0.749 g/cm^3 and 1.45 g/cm^3, respectively. The molar volumes are 345.3 cm^3/mol (Bu_2Mg) and 18.1 cm3/mol (MgH_2). Hence, the reduction in volume would be in the order of a factor of 19, crystalline compounds assumed. This corresponds to shrinkage by a factor of 2.7 in diameter so that pores of 2-3 nm completely filled with Bu_2Mg would contain MgH_2 particles with diameters between 0.7 and 1 nm after the formation step – which was found in the SANS experiments. With this nanocomposite both kinetic and thermodynamic effects were observed.

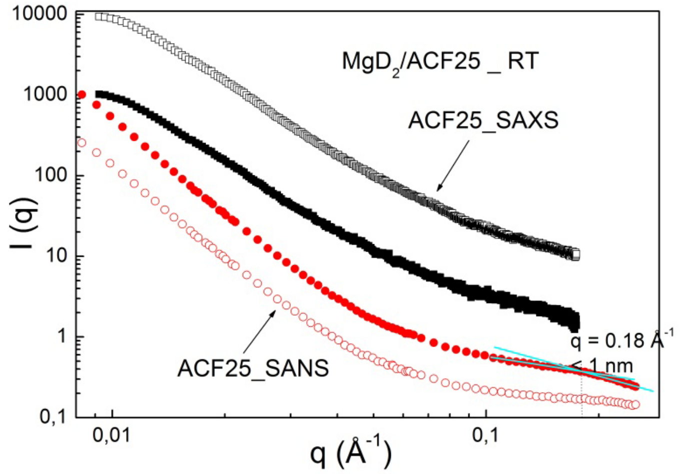


Figure 17: SANS and SAXS on MgD_2 in ACF25.

Hydrogen storage properties

The H_2 storage performance of the nanocomposites generated by WP3 with respect to sorption-desorption capacities, kinetics, thermodynamics, cycle-life, were systematically assessed by a wide range of methods. Also here, the most important results with respect of the nanoconfinement effects were selected and are given in the following.

In most cases, a remarkable difference was detected in the thermal properties and the H storage properties of the material. In general, the **H desorption was largely facilitated** when hydrides were infiltrated in the carbon. However, no H uptake was observed for nanoscale Al which was prepared by decomposing infiltrated AlH_3. The kinetics of the hydrogenation/dehydrogenation were generally enhanced that no catalyst was necessary to perform **equilibrium measurements** with $NaAlH_4$/AC, $NaAlH_4$/ACF-25, and MgH_2/ACF-25.

$NaAlH_4$ dispersed in nanoporous carbon

A study of nanocomposites consisting of natural and artificial activated carbon (average pore diameter 2 nm) infiltrated with $NaAlH_4$ indicated a remarkable difference in the thermal properties of the material. Irrespective of the type of the microporous carbon scaffold, the H desorption was largely facilitated.

In particular, **no catalyst was necessary to perform equilibrium measurements with $NaAlH_4$/AC**. The equilibrium behaviour of the $NaAlH_4$/AC composite differed largely from the one of the catalysed bulk material showing an extended solid solution of H at low pressures and a vanishing of the plateau region. This is the first indication that thermodynamic effects may occur in nanoconfined complex hydrides. The equilibrium behaviour of the $NaAlH_4$/AC composite was reproduced also with other nanocarbon and it could be excluded that impurities in the carbon were responsible for the extraordinary behaviour.

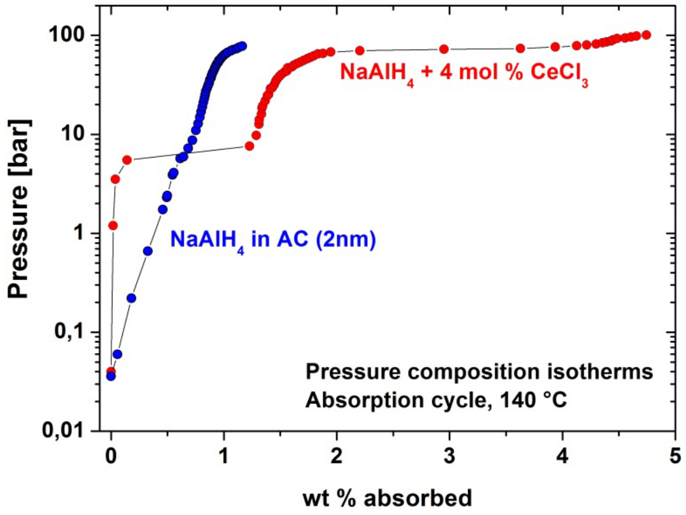


Figure 18: (a) Pressure-composition isotherm (absorption) of $NaAlH_4$ + AC at 140 °C. The upper x-axis shows the absorbed H_2 normalized to the maximum uptake. (b) Comparison of the PCI of ($NaAlH_4$ + AC) with a PCI of $NaAlH_4$ powder catalyzed with 4 m $CeCl_3$.

Figure 18 shows an absorption isotherm of material which was **cycled four times**, compared to the isotherm of a standard material which was catalysed by $CeCl_3$ and measured under the same conditions. It should be noted that cycling is not possible under these conditions with an uncatalyzed $NaAlH_4$ material.

Remarkably, the typical shape observed for bulk $NaAlH_4$ isotherms is lost. The PCI of the composites exhibits a broad distribution of thermodynamic properties whereas for catalyzed bulk $NaAlH_4$ two distinct plateaus are observed, representing the two reaction steps of $NaAlH_4$. To our knowledge, this is the first direct evidence that encapsulation of a complex hydride into a micro- and mesoporous matrix indeed changes the thermodynamic equilibrium state. As can be seen from the Figure, the equilibrium pressure in the low loading region differs by more than an order of magnitude compared to the one of the bulk material.

Obviously, **a facilitated loading of the hydride is observed**, due to altered properties associated with the nanoconfinement of the hydride.

These findings may be of general interest, also for other applications, because, obviously, confinement of a reversible solid state reaction in a void of a few nanometers can lead to altered equilibrium state which is an indication for altered thermodynamics. Hence, the approach may be a promising way to also tune the properties of solid state reaction systems of other energy storage materials, for example.

$Mg(BH_4)_2$ dispersed in nanoporous carbon

Mg borohydride was infiltrated into nanoporous carbon fibre and tested on its thermal properties. Figure 19 shows a TGA-MS experiment which indicates that the hydrogen release already starts at about 160 °C, the first maximum is at 220 °C. The first decomposition step of the bulk hydride occurs at 270 °C under these conditions, the second main event (i.e. decomposition of MgH_2) occurs at 380°C.

Apparently, the various dehydrogenation events which are visible in the bulk material move converge to one broad event in the nanocompositic material which appears to be shifted to lower temperatures. 50 percent of the hydrogen evolution has occurred at 252 K with the nanocomposite, whereas the same amount of desorbed hydrogen was reached at 371 K in the case of the bulk hydride, see Figure 3.

According to this criterion, **the hydrogen desorption temperature was lowered by 120 K in the nanocomposite**.

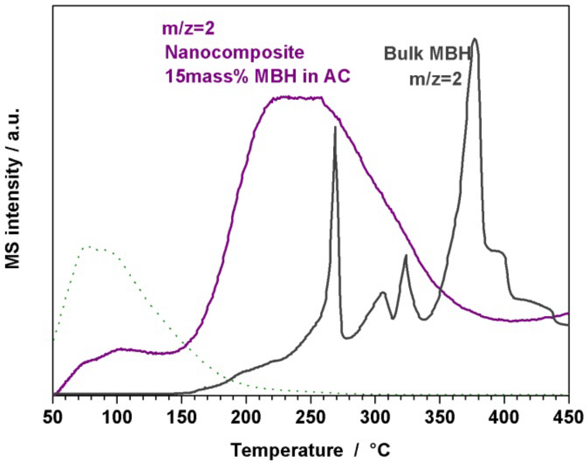


Figure 19: Simultaneous TGA-MS data of $Mg(BH_4)_2$ infiltrated in activated carbon compared to ball milled $Mg(BH_4)_2$.The dotted line is the intensity at m/z=31 (butane).

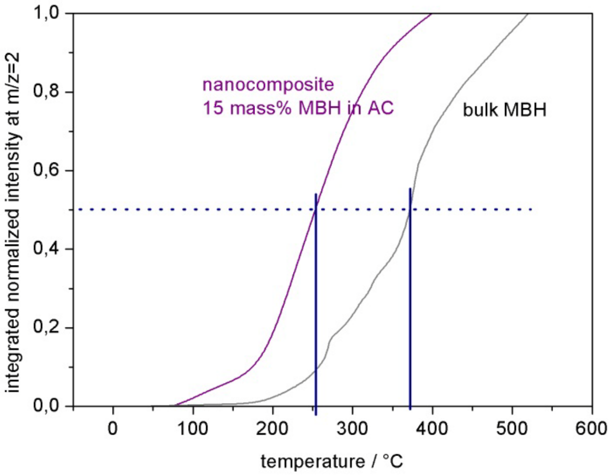


Figure 20: Integrated MS intensity at m/z=2 of $Mg(BH_4)_2$ infiltrated in activated carbon compared to ball milled $Mg(BH_4)_2$.Complete H desorption was assumed at 400 °C for the nanocomposite.

Nanoconfined MgH_2

MgH_2 was incorporated in the micropores of activated carbon fibre by infiltrating dibutyl-magnesium and decomposing the material at elevated temperature under hydrogen atmosphere. Thermogravimetric measurements combined with mass spectrometry of the gas phase (Figure 18) show that the **nanoconfined Mg hydride dehydrogenates at temperatures which are considerably below the decomposition temperature of ball-milled MgH_2.** The difference between the first peak desorption temperature of the nanocomposite the bulk MgH_2 is approximately 100K.

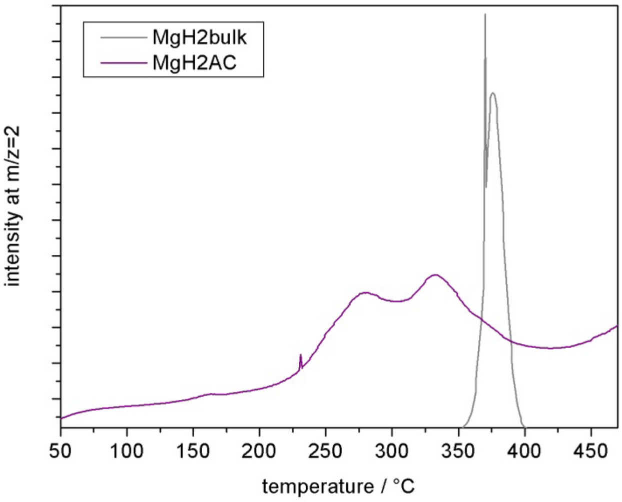


Figure 21: Desorption profiles of simultaneous TGA-MS of MgH_2 confined in activated carbon compared to bulk MgH_2.

Using the 50% desorbed H amount as criterion, desorption of the nanocomposite is shifted by more than 50 K compared to bulk MgH_2, see Figure 19.

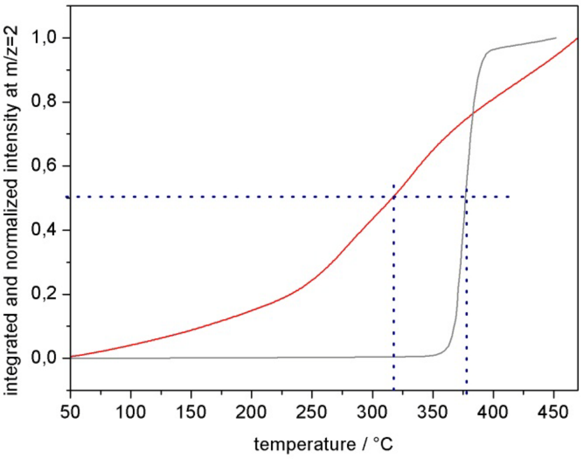


Figure 22: Integrated MS intensity at m/z=2 from TGA-MS experiment of MgH_2 infiltrated in activated carbon (red) compared to ball milled MgH_2 (grey). (Data from Figure 4).

For a more detailed and quantitative investigation of kinetic properties the **apparent activation energy** for hydrogen desorption was estimated by the Kissinger method on the basis of DSC profiles with different heating rates for the as-prepared MgH_2/ACF composite, reference samples of untreated commercial MgH_2 powder, and the ball-milled MgH_2 with graphite, respectively. The Kissinger plots in Figure 18 indicate that both ball-milling MgH_2 with graphite and incorporation of MgH_2 in the nanoporous ACF reduce the apparent activation energy of MgH_2. The largest effect was found with the nanoconfined hydride where the activation barrier of MgH_2 was lowered by 52 and 22 kJ/mol over those of untreated bulk and the ball milled MgH_2 with non-porous graphite, respectively.

The **reduction of activation barriers** can be compared to other work on ball milled MgH_2 which was catalysed by transition metal oxides such as Nb_2O_5 and evaluated by the same kinetic model (Kissinger model). Depending on the study, the activation energy was reduced from either 206 kJ/mol (bulk) to 195 kJ/mol (catalysed) or from 174 kJ/mol to 95 kJ/mol, respectively.

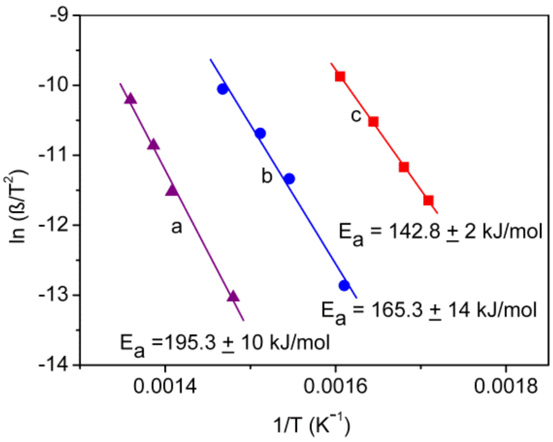


Figure 23: Kissinger plots of the hydrogen desorption reaction of (a) commercial MgH_2; (b) ball-milled MgH_2 with graphite, (c) infiltrated MgH_2/ACF composite.

The **equilibrium pressures of the material were also changed** and pressure-composition isotherm (PCI) measurements at three different temperatures showed enhanced absorption equilibrium pressure of the nanoconfined hydride. Interestingly, the desorption equilibrium pressures were lower which indicates the presence of hysteresis effects with this material.

According to the slope and intercept of the Van´t Hoff plot in Figure 19, the **enthalpy and entropy** of hydride formation for the nanoconfined MgH_2 are **−63.8 ± 0.5 kJ/mol and -117.2 ± 0.8 J/molK**, respectively. The enthalpy of the formation of MgH_2 in ACF matrix is less negative than that of bulk MgH_2 which was determined by the same procedure as −75.7 ± 1.1 kJ/mol. This indicates a **distinctive destabilization** effect for very small MgH_2 particles. Theoretical modelling of MgH_2 nano particles (size ~3 nm) predicted an enthalpy change two times smaller than the experimentally found difference. The reason is probably the even smaller size of the MgH_2/ACF particles as was explained above. An influence of the interface between MgH_2 and the carbon wall is presumably not dominating because it is likely that a big part of the surface of the MgH_2 particles will not interact with the carbon wall, due to the strong shrinkage of the particles during the formation.

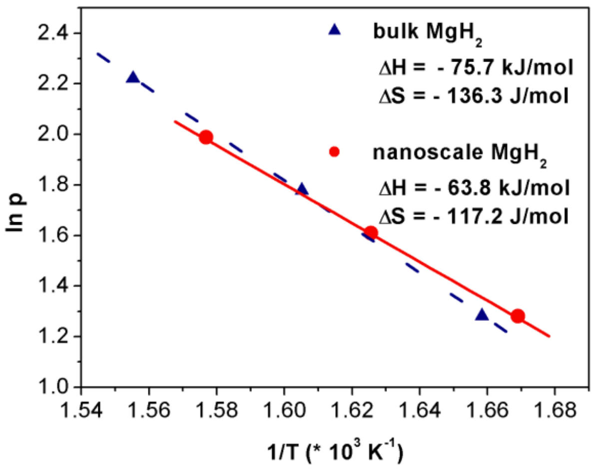


Figure 24: Van't Hoff plot for the formation of MgH_2 in the ACF matrix and the bulk MgH_2 as reference.

Additional infiltrated nano-composite systems have been examined in detail, namely $LiBH_4$-$Mg(BH_4)_2$ infiltrated in the porous carbon material IRH33, CMK infiltrated with $Ca(BH_4)_2$ and CMK infiltrated with $LiBH_4$ composites. In the case of the mixed $LiBH_4$-$Mg(BH_4)_2$/IRH33 composite the thermogravimetric analysis showed not only that the weight loss proceeded in only one step accompanied by hydrogen release at temperatures which are about 50 °C lower than those for bulk material.

Safety studies

The aim of these experiments was to assess potential risk mitigation by lowering the flammability and self-ignition which can be expected from the nano-encapsulation of the complex hydrides.

A strong beneficial mitigation effect was observed when hydrides were encapsulated using the LbL coating technique or the encapsulation in PS shells, as was already shown above (see WP 3). The **stability of sodium borohydride protected by the LbL coating was increased 12 times** compared to the pure material under ambient air conditions.

Alanates infiltrated in nanocarbons and without coatings were comparably reactive to other nanoscale catalysed and ball milled material, however.

In the case of the nano-confined borohydrides, e.g. the mixed $LiBH_4$-$Mg(BH_4)_2$/IRH33 composite the thermogravimetric analysis showed that there was **no diborane released** from the nanocomposite as is shown in the mass spectra of the gas phase.

Evaluation of the nanocomposites

The results of all characterisation steps were collected and processed in order to decide on the most promising nanocomposite system that shall be further used for the upscaling and tank development activities of WP5. For this purpose **$NaAlH_4$ melt infiltrated in microporous IRH-33** was chosen. This combination was selected due to the favorable reversible behaviour of $NaAlH_4$ and the high pore volume of the IRH-33 which was delivered in several 100 gram amounts by Richard Chahine´s group at UQTR in Canada.

4.1.8 Work package 5: Demonstration tank

Objectives of the planned investigations of the work package

At the end of the third year, the collected data was compared and a decision was made for a materials combination for upscale production and for the **laboratory test tank**. Therefore, experiments were carried out for **upscale production of the selected nanocomposite.**

A laboratory setup was constructed for **thermal conductivity measurements** using pelletized nanocomposite samples under inert gas conditions, see Figure 25. Nanocomposites were tested successfully and their thermal conductivity was determined with this setup. The thermal conductivity is a limiting factor in the kinetics of hydride tanks. It must therefore be taken into account in the design of the laboratory tank which was produced and tested by the consortium.

Figure 25: Pictures of the sample holder for thermal conductivity measurements and the thermalized vessel.

A **tank design** was developed and the behaviour of the tank during absorption and desorption processes was simulated. The thermal conduction properties of the $NaAlH_4$ composites used in this study were obtained by measurements on a dedicated apparatus which was constructed for that purpose. **400 g of nanocomposite** were produced at KIT and integrated in the tank at CNRS where it was compacted manually. The tank was integrated in a dedicated test rig and tested under various absorption/desorption conditions. 20 hydrogenation/dehydrogenation cycles were performed with the material which exhibited stable cyclic capacity throughout the tests. The **storage capacity of the composite was approx. 2 mass% H, also during prolonged cycling** which was demonstrated for the first time (see Figure 28). Related to the active material $NaAlH_4$ it was 3.6 mass% H. As demonstration, the tank was connected to a Fuel Cell developed by PaxiTech. The tank was able to supply the Fuel Cell for more than 48 hours.

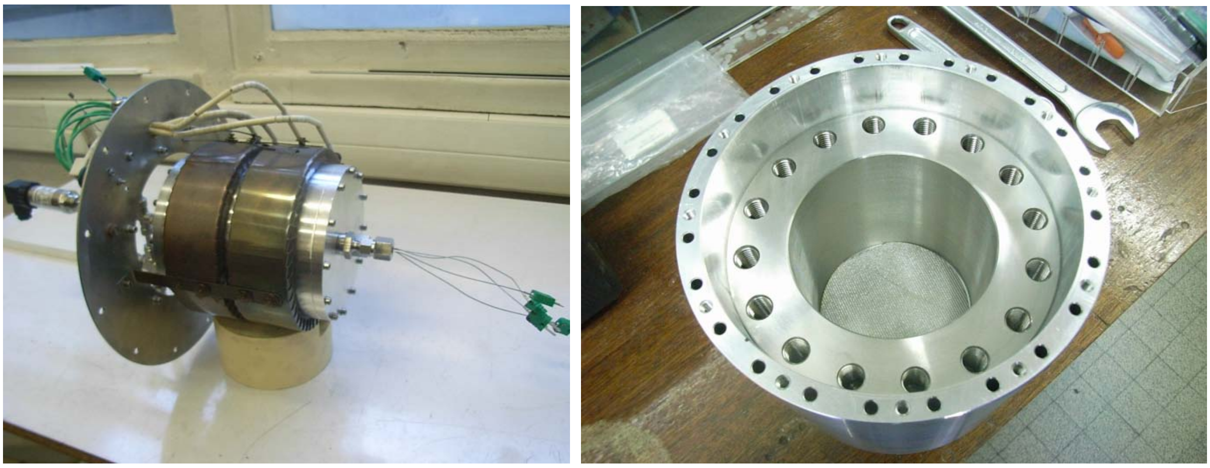


Figure 26: Laboratory test tank built by CNRS.

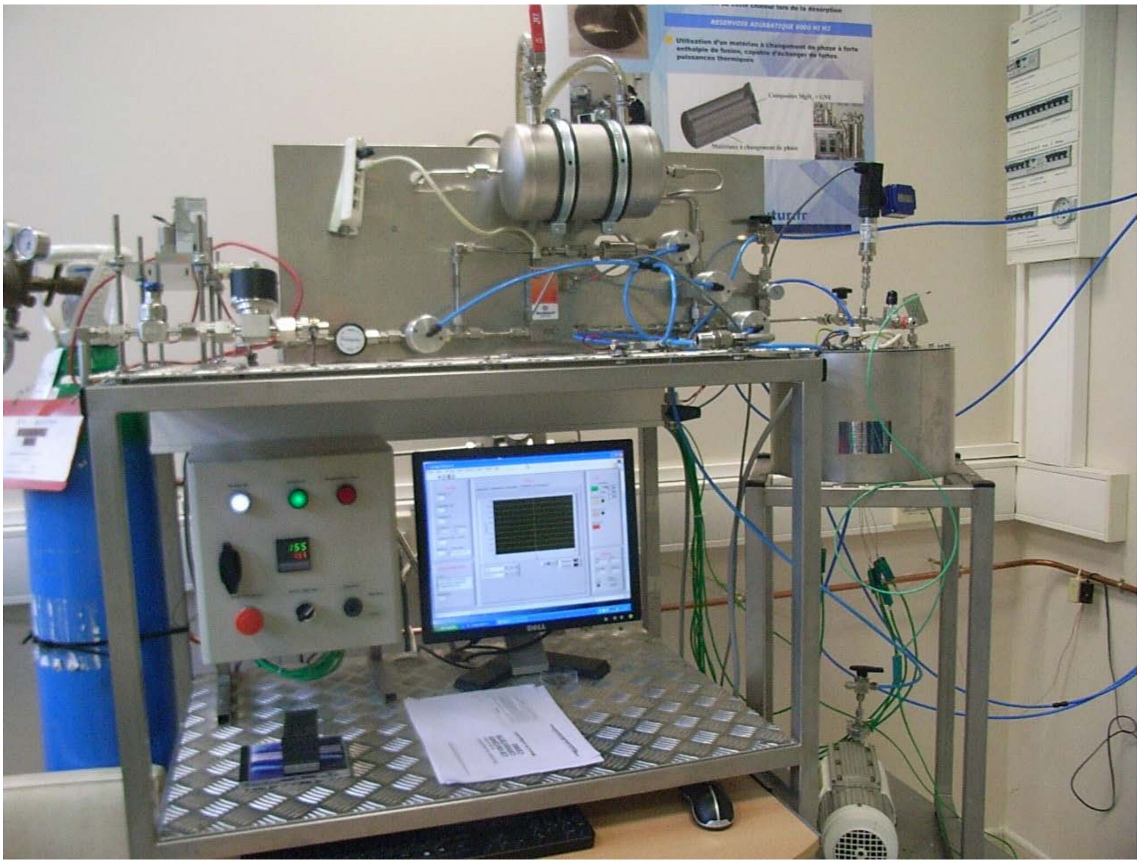


Figure 27: View of the complete test rig, with the insulated tank on the right

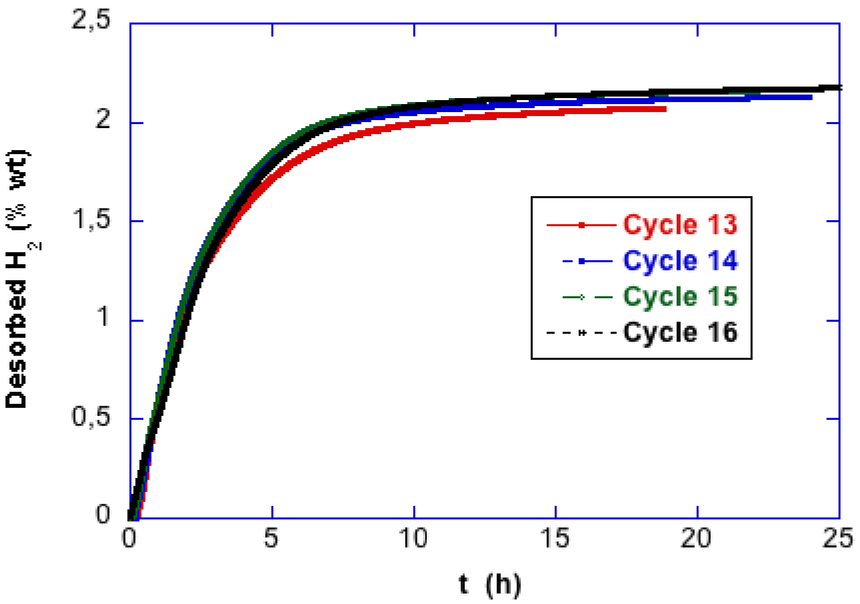


Figure 28: Hydrogen mass desorbed from the material at 150°C (cycles 13 to 16).

In addition, a techno-economical evaluation of the project results was carried out by the industry partner FutureCarbon giving a differentiated view of the scientific-technical results and the commercial perspective in comparison to the state-of-the art.

4.1.9 Main scientific results

The main scientific results with respect to the aims and targets of the project are summarized in brief:

- A knowledge basis was created concerning the properties of complex hydrides on the nanoscale. The main goal to influence materials' properties by scaffolding and nanoconfinement methods has been successfully achieved. In particular the main objectives for materials, processing, modelling, and characterisation techniques were achieved.
- New methods have been developed for the preparation of the composites such as the cryo-infiltration for certain borohydrides. Sophisticated instrumental methods have been introduced for the investigation of the nanoconfined systems such as SANS and INS.
- One of the main results of the project is that it is possible to infiltrate microporous scaffolds by complex hydrides and change their thermodynamic and kinetic properties. A considerable improvement of kinetics was observed with all of the materials investigated. Thermodynamic effects were observed and studied in NANOHy for the first time. These effects are restricted to reversible hydrides and to particles with sizes less than approx. 2 nm, as was proven both by theoretical modeling and experimental measurements. Also other properties change as was successfully predicted by modeling and demonstrated by experiments.
- Not possible in the course of the project was changing the reaction pathway such that irreversible bulk hydrides would become reversible. Hence, no improvement of reversible storage capacities was achieved by using such types of hydrides (e.g. AlH_3, $Mg(BH_4)_2$).
- The reactivity in air can be lowered considerably by nanocoatings produced by the layer-by-layer technique or by application of thin polystyrene coatings.

- An upscale production of 400 g nanocomposite was done for the first time and a suitable laboratory tank was developed for a $NaAlH_4$/AC nano-composite composite. The material can be cycled without further addition of catalyst and exhibits a good cyclic stability.
- The gained knowledge shall and will be transferred in the sense of a spin off also to other functional materials. It is intended to use similar techniques for the application in battery materials where a carbon matrix is not only adding dead weight to the system but is also necessary to provide electronic transfer from and to the active materials particles of the electrodes.

4.1.10 Potential impact (including the socio- economic impact and the wider societal implications of the projects so far) and the main dissemination activities and exploitation of results

4.1.10.1 Potential impact and exploitation of results

One of the most important challenges of the European Community is the implementation of new energy concepts into a well developed "technical orientated" Society. There exists no doubts about the necessity of new energy concepts, but this implements the use of various energy carriers. One of the most promised energy carrier for a European future is "hydrogen". The focus of NanoHy was clearly concerning that line, while developing and investigating new nano-composite based hydrogen storage materials. An up scaling of the material ($NaAlH_4$/AC nano-composite) and test under real conditions reflects that the new storage material could close the technical gap of mobile and stationary applications, while expanding the capacity of storable hydrogen within a tank. Above all, the material shows excellent properties regarding recycling (recycle-able without further addition of catalyst) and exhibits a good cyclic stability. The knowledge will be transferred in the sense of a spin off also to other functional materials. It is intended to use similar techniques for the application in battery materials where a carbon matrix is not only adding dead weight to the system but is also necessary to provide electronic transfer from and to the active materials particles of the electrodes.

The work plan and the activities in NANOHy was focused on achieving scientific breakthroughs in a new field which is regarded as one of the very rare options to alter thermodynamic and kinetic properties of functional materials. Achieving breakthroughs is of particular importance for energy storage especially for mobile and automotive applications because both in hydrogen storage and in electrochemical storage there is a lack of systems with "ideal" properties. Ideal in that respect means that a material with very high energy storage capacity operates fast and reversible at moderate temperature and pressure conditions (H storage) or that an electrode material (batteries) is embedded safely and stable in an electrically conducting matrix thus enabling a good electronic transfer during charging and draining which is prerequisite for enhanced cyclic stability. Moreover, the active material should have low kinetic barriers for transformation during Li uptake and release which is a precondition for low overpotentials and high roundtrip efficiency.

In total, NANOHy was able to demonstrate theoretically and experimentally the correctness and feasibility of the scientific approach of nanoconfinement; the consortium was also able to present a world-first demonstrator tank which showed that the laboratory concept can be scaled up. The nanoconfined complex hydride which was prepared showed considerably improved kinetic properties so that no catalyst was necessary, and it exhibited stable cycle behavior during the several tens of cycles of the test phase.

During the course of the project the focus of the work was on the development of

- Novel preparation techniques for nanoconfined systems
- Novel methods for investigation of nanoconfined systems
- Understanding of the underlying principles of the altered properties

Hence, the strategy for dissemination in NANOHy was chosen according to the above-mentioned aims of the project and the state of knowledge in the field.

In order to protect the knowledge gained by the partners at this early stage of development it was planned to not only publish scientific achievements and offer them to the scientific and industrial community. In addition, the consortium also collected and discussed critical and potentially protectable results in a series of confidential reports and deliverables. As it turned out during the project period especially specific knowledge and skills for the synthesis of nanocomposites was essential for the successful preparation of highly functional systems. However, it was not the major aim of the project to proceed to patent applications but rather to demonstrate the feasibility of the technology while at the same time disseminating it widely enough so that its applicability in hydrogen storage and other fields (batteries) is ensured.

Therefore, while no patents were actually obtained, the techniques and the work was treated as non-protectable know-how which is a frequent and common element in partnerships between industry and research. In fact, NANOHy has developed into an esteemed contact and discussion partner in the community which is also proven by a series of invited lectures and visits of international researchers to members of the consortium.

Overall, the strategy of dissemination has been to multiply, expand and strengthen the gained knowledge in the scientific/technical community in order to achieve a broader basis for further scientific achievements and technical development. It is obvious that the results which have been published in a series of conference talks, posters, and scientific publications in international refereed journals have already stimulated a lot of follow-up research as is evident from the scientific-technical literature. An important success of this strategy has been the recent observation that groups working also on functional materials other than metal hydrides have started to develop related strategies in order to tune or optimize materials properties. Meanwhile, the first groups working on battery materials have successfully applied the techniques and scaffold materials first presented in NANOHy to considerably improve the properties of the Li-S battery, the development and commercialization of which is currently one of the most important targets for the storage of electrical energy [see, e.g. D. Aurbach *et al.*, Adv. Mater, 2011]. Another promising example is the upcoming use of metal hydrides as high capacity anodes in Li ion batteries where they are in contact with non-aqueous electrolyte thus avoiding a detrimental reaction with protonic media as it would be the case in a Ni-MH battery [e.g. S. Brutti *et al.*, J. Mater. Chem. 22 (2012) 14531]. Also here, nanoscale dispersion is favorable and because ball-milled materials are structurally not stable during electrochemical cycling the approach of nanoconfinement can lead to stabilization and better electrical contact of the reacting phase.

As a consequence, NANOHy has decided to expand its initial strategy and to disseminate the knowledge further by keeping the project website available to the public and expanding its information content. This shall be achieved by transferring the content of the website to the H2FC portal, which is also operated by KIT, the co-ordinator of H2FC. Furthermore, NANOHy shall disclose the formerly confidential reports, namely the Deliverables 1.1-1.9, D 3.1-3.5, D 4.1-4.2, D 5.1-5.2, 5.4, 5.6, D 6.3-6.4, 6.8-6.10 which is 25 reports in total. The reports shall be made accessible together with the other reports which are already public.

Another important strategy for dissemination in the future will be to further transfer the modeling, preparation and measurement techniques to other functional materials. As already mentioned above, battery materials seem to be a particular attractive option because the nanoporous scaffold which is necessary to obtain and stabilize the nanoscale dispersion does not only contribute in weight and therefore compromises the energy density of the storage system to a certain extent like in H storage materials – in batteries, electrically conductive carbon is necessary to provide a percolating structure of electrical conduction pathways in the electrodes, which means the use of carbon is anyhow compulsory.

It should be stressed that in this context the NANOHY team has already started discussions on how to transfer the know-how obtained up to now in the development of advantageous, optimized materials for electrochemical storage as well. It is the aim of the partners in NANOHy to apply for and collaborate in further projects where the effects of nanoconfinement shall be investigated and applied to the development of novel electrode materials. The consortium would appreciate if the world-class expertise of the partners in the field could be utilized in the upcoming EC research and funding programs.

4.1.10.2 Main dissemination activities

The main dissemination activities regarding NanoHy consisted of scientific publications in several high ranked journals and additionally a number of oral presentations and posters presented at conferences and workshops:

Publications done by KIT

- M. Fichtner, *Properties of Nanoscale Metal Hydrides*, Nanotechnology 20 (2009) 204009
- M. Fichtner, Zh. Zhao-Karger, J. Hu, A. Roth, P. Weidler *Kinetic Properties of* $Mg(BH_4)_2$ *Infiltrated in Activated Carbon*, Nanotechnology 20 (2009) 204029
- M. Fichtner, *Conversion materials for hydrogen storage and electrochemical applications - concepts and similarities*, J. Alloys Compd. 509S (2011) S529 – S534
- A. Ampoumogli, Th. Steriotis, P. Trikalitis, D. Giasafaki, E. Gil Bardaji, M. Fichtner and G. Charalambopoulou, *Nanostructured composites of mesoporous carbons and boranates as hydrogen storage materials*, J. Alloys Compd. S509 (2011) S705-S708.
- A. Giannasi, D. Colognesi, L. Ulivi, C. Ziparo, M. Zoppi, A. Roth, and M. Fichtner, *Temperature behavior of the* AlH_3 *polymorph by in-situ investigation using high resolution Raman scattering*, J. Phys. Chem. A 115 (5) (2011) 691-699.
- E.G. Bardají, Zh. Zhao-Karger, N. Boucharat, A. Nale, M.J. van Setten, W. Lohstroh, E. Röhm, Michele Catti and M. Fichtner, $LiBH_4$-$Mg(BH_4)_2$*: A Physical Mixture of Metal Borohydrides as Hydrogen Storage Material*, J. Phys. Chem. C 115 (2011) 6095-6101.
- D. Colognesi, A. Giannasi, L. Ulivi, M. Zoppi, J. Ramirez-Cuesta, A. Roth, M. Fichtner, *Raman and Inelastic Neutron Scattering Study on a Melt-Infiltrated Composite of Sodium Aluminum Tetrahydride and Nano-Porous Carbon*, J. Phys. Chem. A *115* (26) (2011) 7503–7510
- M. Fichtner, *Nanoconfinement effects in energy storage materials*, Phys. Chem. Chem. Phys. 13 (2011) 21186-21195
- P. Vajeeston, P. Ravindran, M. Fichtner, H. Fjellvåg, *Influence of the crystal structure of bulk phase on the stability of nanoscale phases: Investigation of* MgH_2 *derived nanostructures,* Chem. Materials (submitted Oct. 12, 2011)

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- M. Fichtner, Wiebke Lohstroh, Arne Roth, Zhirong Zhao-Karger, *Tailoring of Nanocomposite Materials for Hydrogen Storage*, AAAS Annual Meeting, February 12-16, 2009, Chicago, USA
- M. Fichtner, *Nanomaterials for Energy Applications - Challenges and prospects*, EuroNanoForum 2009, 2-5 June, Prague, Czech Republic
- M. Fichtner, *Three lectures about Chemistry and Physics of Materials for Energetics*. European School in Materials Science, University of Milano-Bicocca; Milano, 14-19 September 2009
- Wiebke Lohstroh, Arne Roth, Zhirong Zhao-Karger, Maximilian Fichtner, *Thermodynamic properties of* $NaAlH_4$ *– AC composites*, SSHS Int. Workshop, 10.-11.6.2009, Heraklion/Greece.
- Zhirong Zhao-Karger, Maximilian Fichtner, Jianjiang Hu and Arne Roth, *Enhanced Hydrogen Desorption Kinetics of* $Mg(BH_4)_2$ *Infiltrated in Nanoporous Carbon Scaffolds*, SSHS Int. Workshop, 10.-11.6.2009, Heraklion/Greece.
- Jianjiang Hu, Zhirong Zhao-Karger, Wiebke Lohstroh and Maximilian Fichtner, *Utility of Reactions between* $LiNH_2$ *and* MgH_2 *for the hydrogen storage purpose*, SSHS Int. Workshop, 10.-11.6.2009, Heraklion/Greece

- Zhirong Zhao-Karger, Arne Roth, Jianjiang Hu, Maximilian Fichtner, *Chemical Preparation and Hydrogen Sorption Properties of MgH_2/Carbon Nanocomposites*, SSHS Int. Workshop, 10.-11.6.2009, Heraklion/Greece.
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- S. Sartori, K. D. Knudsen, Zh. Zhao-Karger, E. G. Bardají, J. Muller, M. Fichtner, B. C. Hauback, Nano-confined Mg-borohydride for hydrogen storage applications investigated by SANS and SAXS, J. Phys. Chem. C 114 (2010) 18785-18789
- M. Fichtner, Synthesis and properties of nanocomposites based on tetrahydroborates, CIMTEC 2010, June 14-18, Montecatini, Italy [Talk]
- M. Fichtner, Conversion materials for hydrogen storage and electrochemical applications - concepts and similarities, Plenary Talk, Int. Symposium on Metal-Hydrogen Systems (MH 2010), July 19-23, 2010, Moscow, Russia [Talk]
- M. Fichtner, Hydrogen and batteries for energy storage in automobiles, Workshop structure analysis for automotive components, 26.10.2010, Stuttgart, Germany [Talk]
- M. Fichtner, Nanomaterials for Energy Applications - challenges and prospects, VDE Kongress, 8.-9. Nov. 2010, Leipzig, Germany [Talk]
- M. Fichtner, R. Prakash, A. Roth, Z. Zhao-Karger, W. Lohstroh, Kinetic and Thermodynamic Properties of Nanoconfined Materials for Energy Storage, MCRTN conference on Nano- and Surface Science Approaches to Production and Storage of Hydrogen, 14.-19. Nov. 2010, Leiden University, NL [Talk]
- M. Fichtner, Ch. Frommen, A. Léon, W. Lohstroh, Alanates - Synthesis, Transformation Mechanism and Technical State of the Art. 4th Hydrogen & Energy Symposium, Jan 24-29, 2010, Wildhaus, Switzerland [Talk]
- W. Lohstroh, A. Roth, and M. Fichtner, Thermodynamic Properties of NaAlH4 /Activated Carbon Fibre Composites, 1st Intern. Conference on Materials for Energy, July 4-8, 2010, Karlsruhe [Talk]
- A. Giannasi, D. Colognesi, L. Ulivi, M. Zoppi, E.G. Bardaji, E. Roehm, A. Roth, Z. Zhao-Karger, M. Fichtner, A. J. Ramirez-Cuesta, High resolution Raman and neutron study of complex hydrides: Mg(BH4)2 and NaAlH4, Int. Symposium on Metal-Hydrogen Systems, July 19-23, 2010, Moscow, Russia [Talk]
- W. Lohstroh, A. Roth, and M. Fichtner, Tailoring Thermodynamics in NaAlH4-activated carbon fibre composites, Int. Symposium on Metal-Hydrogen Systems, July 19-23, 2010, Moscow, Russia [Talk]

Publications done by IFE

- S. Sartori, K. D. Knudsen, Zhirong Zhao-Karger, M. Fichtner, B.C. Hauback , Nanoparticle infiltration of Mg-borohydride in activated carbon, Nanotechnology 20 (2009) 505702.

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- S. Sartori, K.D. Knudsen, Z. Zhao-Karger, M. Fichtner, B.C. Hauback, Complex hydrides in carbon nanoscaffolds. Gordon Research Conference Hydrogen-Metal Systems, Italy, July 2009.

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- 2012: Sabrina Sartori, invited talk, *Influence of carbon nanostructures on metal hydrides for hydrogen storage applications*, Materials Challenges in alternative and renewable energy, MCARE, Clearwater Beach, Florida, USA, February 26-March 1.
- 2011: Sabrina Sartori, invited talk, *Nanoconfined hydrides for hydrogen storage*, International Conference on Advanced Materials, ICAM-2011, Coimbatore, India, December 12-16.
- 2011: Sabrina Sartori, K.D. Knudsen, B.C. Hauback, invited talk, *Nanoscaled hydrides in carbon scaffolds: the role of small-angle scattering*, Low Carbon Earth Summit, LCES-2011, Dalian, China, October 19-26.
- 2011: Sabrina Sartori, invited talk, *Nanoscaled hydrides in porous scaffolds: the role of small-angle scattering*, Gordon Research Conference (GRC) "Hydrogen-Metal Systems", Stonehill College, USA, July 17-22.
- 2011: Sabrina Sartori, Lecture at Department of Physics and Astronomy, Materials Physics, Uppsala University, Sweden, February 2011.
- 2011 Sabrina Sartori, K.D. Knudsen, B.C. Hauback, Poster, *The role of small-angle scattering in the investigation of nanoscale hydrides in carbon scaffolds*, Geilo Schools, Norway, 4-14 April 2011.
- 2011: Sabrina Sartori, K.D. Knudsen, B:C: Hauback, Poster, *The role of small-angle scattering in the investigation of nanoscaled hydrides in carbon scaffolds for hydrogen storage applications*, 1st Niels-Bohr International Academy Workshop-School on ESS Science, Niels Bohr Institute, Copenhagen, Denmark, June 27 – July 1.
- December 2010-January 2011: Sabrina Sartori, Visiting researcher at DIM, University of Padova, Italy.
- 2010: Sabrina Sartori, talk *Small-angle neutron scattering investigations of hydrides for hydrogen storage applications*, Technical Meeting of IAEA, Trois-Rivières, Quebec, Canada, 23-26 August.
- 2010: Sabrina Sartori, talk *Nanosized complex hydrides in carbon scaffolds*, MH2010, Moscow 19-23 July.
- 2010: Sabrina Sartori, Lecture at the *Neutron scattering methods for materials research*, course FYS9440 of University of Oslo, Kjeller, IFE, September 20-24
- 2010: Sabrina Sartori, 2 Lectures at the *Summer School* on hydrogen, University of Reykjavik Reykjavik, Iceland, August 17-21.

- 2010 Sabrina Sartori, Poster, *Small angle scattering on nano-confined hydrides for hydrogen storage*, International School of Solid State Physics on “Materials for Renewable Energy”, Ettore Majorana Foundation and Center for Scientific Culture, Erice, Italy, May 27 – June 3.

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- F. Grazzi, A. Scherillo, M. Zoppi; *A neutron imaging device for sample alignment in a pulsed neutron scattering instrument*, Rev. Sci. Instrum.80 (2009) 93704
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- M. Ceriotti, G. Miceli, A. Pietropaolo, D. Colognesi, A. C. Nale, M. Catti, M. Bernasconi e M. Parrinello, *Nuclear quantum effects in ab initio dynamics theory and experiments for lithium imide*, Phys. Rev. B **82** (2010) 174306
- A. Giannasi, D. Colognesi, M. Fichtner, E. Röhm, L. Ulivi, C. Ziparo, and M. Zoppi; Temperature *Behavior of the AlH3 Polymorph by in Situ Investigation Using High Resolution Raman Scattering*, J. Phys. Chemistry A, v. **115**, p. 691 (2011)
- D. Colognesi, A. Giannasi, L. Ulivi, M. Zoppi, A. J. Ramirez-Cuesta, A. Roth, M. Fichtner; *Raman and inelastic neutron scattering study on a melt-infiltrated composite of sodium aluminum tetrahydride and nano-porous carbon*, J. Phys. Chemistry A, v. **115**, p. 7503 (2011)
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- M. Zoppi, M. Celli, D. Colognesi, A. Giannasi, L. Ulivi: *Thermal neutrons investigation of materials for hydrogen storage*, Contributed Talk by M. Zoppi, IAEA – Technical Meeting, (Paris, F, 16-20 March 2009).
- M. Zoppi: *Microscopic characterization and modeling of H-storage materials by Raman spectroscopy and neutron scattering*, IEA HIA – Task 22: Expert Meeting (Paris, F, 11-15 Oct. 2009).

- M. Zoppi, *Immagazzinamento dell'idrogeno: un nodo cruciale per il suo efficace utilizzo come vettore energetico,* 2nd International exibition of advanced solutions and technologies for Research, Science and Industry (Milano, Italy, 25-27 Nov. 2009)
- Giannasi, D. Colognesi, L. Ulivi, M. Zoppi, A. J. Ramirez-Cuesta, E. G. Bardaji, E. Röhm, M. Fichtner; *High resolution Raman and neutron investigation of Mg(BH4)2 in an extensive temperature range*, J. Phys. Chemistry A **114** (2010) 2788-2793.
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- M. Celli, D. Colognesi, A. Giannasi, L. Ulivi, M. Zoppi: *Simple and Binary Hydrogen Clathrate Hydrates: Synthesis and Microscopic Characterization Through Neutron and Raman Scattering;* Invited Lecture by M. Celli at FB Symposium (MATERIALS AND PROCESS INNOVATIONS IN HYDROGEN PRODUCTION AND STORAGE), 5th Forum on New Materials (CIMTEC 2010, Montecatini Terme, Italy, 13-18 *June* 2010). [Talk]
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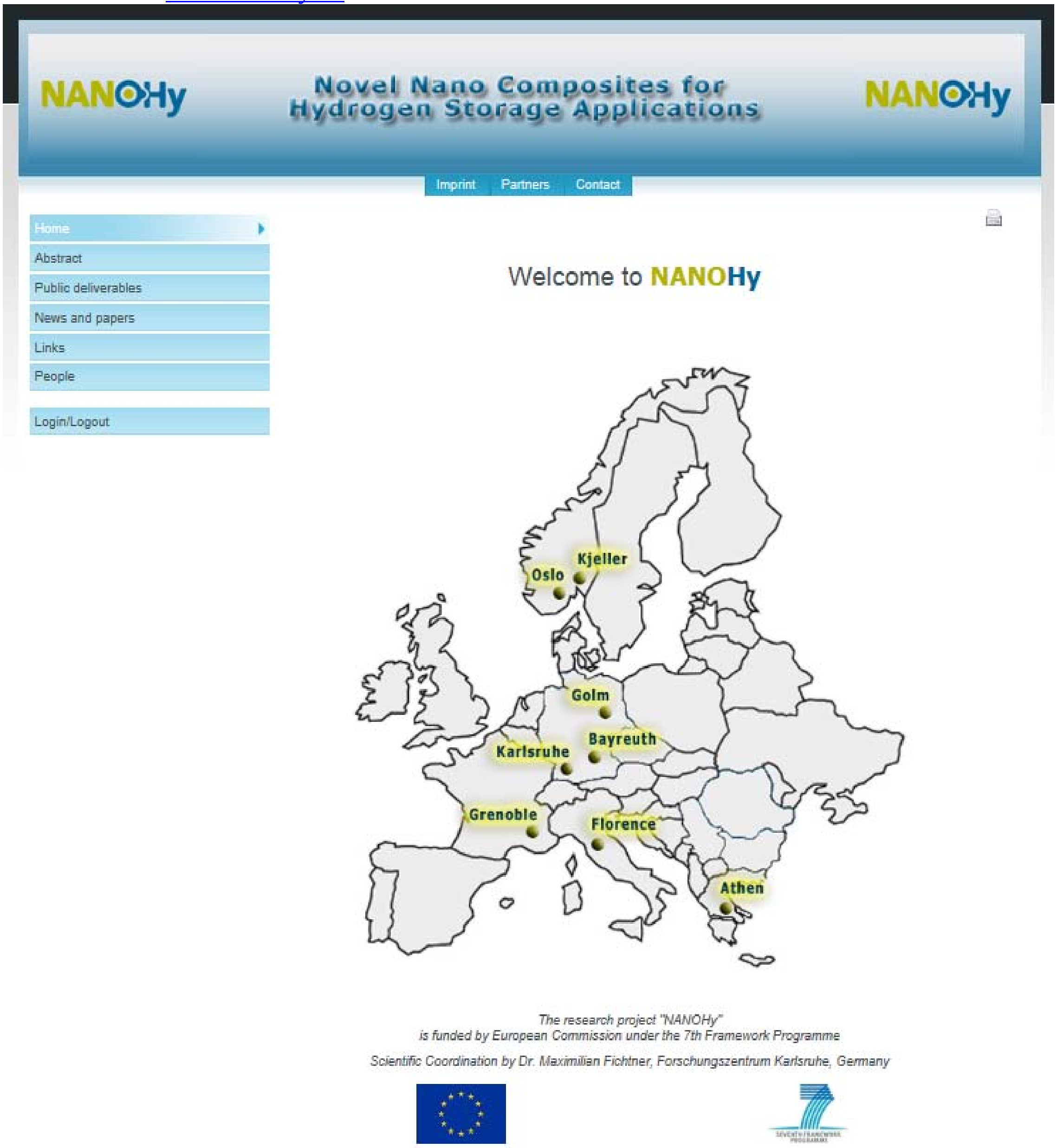
4.1.11 Public website of the project and relevant contact details concerning NanoHy

Public website www.nanohy.eu



Welcome to NANOHy

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