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Summary

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1 ABSTRACTS TALKS

NANOMAT2012, September 30 - October 7, Sao Carlos, Brasil

Mg-based transition-metal complex hydrides produced by reactive milling

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In this work, we employed ball milling in a reactive H_2 (or D_2) atmosphere to explore the possibility of producing quaternary Mg-based transition-metal complex hydrides. The results focus on Mg-Fe-Co and Mg-Mn-Fe systems and were compared with preliminary data for ball milled Mg-Mn-Co and Mg-Mn-Ni powders. The aim is exploring if: i) different transition-metal complex anions, such as $[FeH_6]^{4-}$ and $[CoH_5]^{4-}$, can coexist in the same crystalline structure and ii) the presence of $[FeH_6]^{4-}$, $[CoH_5]^{4-}$, or $[NiH_4]^{4-}$anions can stabilize the $[MnH_6]^{5-}$ complex, which is observed in Mg_3MnH_7 prepared at high pressure (2 GPa) and temperature (800 K).[1]

Elemental powder mixtures were ball milled in H_2 (or D_2) at about 50 bar. The structural characterization of the powders was carried out by powder diffraction analysis and vibrational spectroscopy (i.e. IR). The thermal stability and the hydrogen sorption behaviour were investigated by differential scanning calorimetry and thermal programmed desorption. In-situ powder diffraction was carried out to follow the structural changes upon heating and hydrogen desorption.

It was found that the quaternary hydride $Mg_2(FeH_6)_{0.5}(CoH_5)_{0.5}$ forms during reactive milling and adopts a K_2PtCl_6-type structure (space group $Fm3m$, $a \approx 6.42$ Å). This confirms that the two different transition metal complex anions $[FeD_6]^{4-}$ and $[CoD_5]^{4-}$ can coexist in the same crystalline structure. Hydride phases with a cubic K_2PtCl_6-type structure with lattice parameter a up to 6.45 Å are observed also in the Mg-Mn-Fe systems, but evidence of the formation $[MnH_6]^{5-}$ complexes could not be found. Investigations of the hydrogen desorption upon heating suggest the presence of Mn can have a destabilization effect on the thermal stability of hydride phases. These results are discussed and compared with new data for Mg-Mn-Co and Mg-Mn-Ni powders.

[1] M. Bortz, B. Bertheville, K. Yvon, E.A. Movlaev, V.N. Verbetsky, F. Fauth, J. Alloys Compd. **279**, (1998) L8.

"MHS- Future Perspectives?", June 14-18, Norwegian Coastal Express
&
MH2012, October 21-26, Kyoto, Japan

Mg-based Mixed Transition-Metal Complex Hydrides Obtained by Reactive Milling

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Ball milling techniques are considered beneficial for processing potential hydrogen storage materials. This is due to the grain-size reduction process, which occurs during the continuous fracturing and cold welding of the powder particles and results in improved H-sorption kinetics.[1] At the same time, ball milling allows to mechanically mix elements/compounds at an atomic scale, extend the solid solubility of metals and, in turn, obtain novel materials that might show interesting hydrogen storage properties.[2]

In this work, we employed ball milling in a reactive H_2 (or D_2) atmosphere to explore the possibility of producing quaternary Mg-based transition-metal complex hydrides. The results focus on Mg-Fe-Co and Mg-Mn-Fe systems and were compared with preliminary data for ball-milled Mg-Mn-Co and Mg-Mn-Ni powders. The aim is exploring if: i) different transition-metal complex anions, such as $[FeH_6]^{4-}$ and $[CoH_5]^{4-}$, can coexist in the same crystalline structure and ii) the presence of $[FeH_6]^{4-}$, $[CoH_5]^{4-}$, or $[NiH_4]^{4-}$ anions can stabilize the $[MnH_6]^{5-}$ complex, which is observed in Mg_3MnH_7 prepared at high pressure (2 GPa) and temperature (800 K).[3]

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References

[1] A. Zaluska, L. Zaluski, J.O. Ström-Olsen, J. Alloys Compd. 288 (1999) 217.
[2] J. Huot, S. Boily, E. Akiba, R. Schulz, J. Alloys Compd. 280 (1998) 306.
[3] M. Bortz, B. Bertheville, K. Yvon, E.A. Movlaev, V.N. Verbetsky, F. Fauth, J. Alloys Compd. 279 (1998) L8.

“MHS - Future Perspectives ?”, June 14-18, Norwegian Coastal Express
&
SYNKNØYT, Stavanger, Norway

The “not-so-common” Borohydrides: Crystal Structure and Thermal Properties.

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Organic complexes and solvent adducts of rare-earth borohydrides are widely used as highly selective reducing agents for various types of chemical reactions. In addition, purely inorganic and solvent-free borohydrides are currently heavily researched. They are considered very attractive materials for hydrogen storage applications due to their high gravimetric H-densities ($LiBH_4$: 18.5 wt. %).Whereas the structures of the alkali, alkaline earth and few 3d-transition metal borohydrides are well established by now, very little is known about the borohydrides formed by the heavy elements in the periodic table. With the exception of $RE(BH_4)_3$ (RE =Y, Ce, Gd and Dy), no information about other members of the 4f-elements forming similar compounds can be found in the literature.

This presentation will report on our recent efforts in synthesizing novel rare-earth borohydrides, and their characterization with synchrotron radiation and neutron powder diffraction experiments. Selected examples include $LiCe(BH_4)_3Cl$: the first mixed-metal and anion substituted rare-earth borohydride; $Tb(BH_4)_3$ and $Er(BH_4)_3$: two new members of the rare-earth borohydride family, and other products obtained from mechano-chemical reactions between $LiBH_4$/KBH_4 and chlorides of the rare-earth elements Eu, Tb, Er and Yb.

In particular, the mechanochemical reaction between $3LiBH_4$ and $YbCl_3$ has resulted in the formation of several phases. Short reaction times yield an unknown phase which could be a Li-Yb-(BH_4)-Cl containing compound that transforms into $Yb(BH_4)_3$ and LiCl after longer reaction times. $Yb(BH_4)_3$ shows polymorphism similar to $Y(BH_4)_3$ and forms α-$Yb(BH_4)_3$ (Pa-3; $a \approx 10.75$ Å) and β-$Yb(BH_4)_3$ (Fm-3c; $a \approx 10.9$ Å). In addition to the crystal structure, some emphasis will be on the thermal properties of rare-earth borohydrides, e.g. decomposition path followed by in-situ SR-PXD at the Swiss-Norwegian Beamline (SNBL) at ESRF, hydrogen desorption/absorption behavior etc.

ECM27 - The 27th European Crystallographic Meeting, August 6-11, Bergen, Norway

Changing Properties of Hydrogen Storage Materials by Halide Substitution.

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The search is ongoing to find clean and renewable energy systems. Hydrogen is an attractive energy carrier, since only water is formed when hydrogen is reacting with oxygen to release energy in a fuel cell or combustion engine. One of the main problems for hydrogen to become an effective energy carrier is to find effective ways to store hydrogen in vehicles or stationary storage units. Hydrogen fails to meet the demands to volumetric density set by e.g. US DoE even when stored under high pressure or condensed to a liquid at low temperature. A safer and more compact way is to store hydrogen in solid compounds, e.g. in metal hydrides such as MgH_2 and $LaNi_5H_6$. Bogdanovic discovered in 1997 that the complex metal hydrides, $NaAlH_4$, can store hydrogen reversible by adding a dopant, $TiCl_3$[1]. A lot of focus has been given to alanate ($M_n(AlH_4)_m$), but lately more attention has been given to borohydrides ($M_n(BH_4)_m$) that contains more hydrogen per unit weight. The properties of both alanates and borohydrides can be changed by substituting part of the compound with different ions. Hydrogen in alanate can be substituted with fluorine [3], and the whole BH_4 group in borohydrides can be substituted with Cl, Br or I [4]. Substitution changes the hydrogen release properties, and can therefore be used to tune these properties. In this work, we have investigated possible substitution in $Ca(BH_4)_2$ with CaF_2, $CaCl_2$ and $CaBr_2$. $Ca(BH_4)_2$ has several polymorphs, α-$Ca(BH_4)_2$ is stable at room temperature. Above 200 °C the β-phase is more stable. α- $Ca(BH_4)_2$ crystallizes in the orthorhombic, space group *F*2*dd*, while β-$Ca(BH_4)_2$ crystallizes in the tetragonal space group *P*42/*m*. After ball milling α-$Ca(BH_4)_2$ with $CaCl_2$, no change is seen in the unit cell axes of α-$Ca(BH_4)_2$, indicating that no substitution takes place. The evolution with temperature was studied using in-situ synchrotron powder diffraction at SNBL, ESRF in Grenoble, France. At 150-200 °C, the α-phase is transformed into the β-$Ca(BH_4)_2$, then at about 250 °C the Bragg peaks of the β-phase are shifted to higher angles, indicating shrinkage of the unit cell volume, in agreement with substitution of smaller Cl^-. Substitution is seen with heat treatment of ball milled $Ca(BH_4)_2$ + $CaCl_2$ with ratio 1:0.5, 1:1, 1:2, giving $Ca((BH_4)_{1-x}Cl_x)_2$, where x varies with the ratio. No substitution was observed with CaF_2 and $CaBr_2$.

[1] Bogdanovic, B et. al. (1997) *J. Alloys compd.* **253-4** : 1-9 [2] Ronnebro, E et. al (2007) *J. Phys. Chem.* **111** 12045-47 [3] Brinks, H. W. et. al. (2008) J. Phys. Chem. **112** : 5658-61 [4] Rude, L. H. et. al. (2011) *J. Phys. Chem.* **115** : 7768-77

Keywords: Hydrogen Storage; In-Situ Synchrotron Powder Diffraction; Substitution

MH2012, October 21-26, Kyoto, Japan

Ball milling of Mg with Ti/Zr in a reactive hydrogen (deuterium) atmosphere

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Based on thin films studies it has been shown that Mg-Ti-H system reveals high hydrogen storage capacity and very good electrochemical performance. The obtained hydride with the fluorite-type structure can store hydrogen reversibly up to ~ 6.5 wt.% [1]. So far studies on a bulk material have not confirmed such outstanding properties [2, 3]. On the other hand, the ternary hydride with FCC-type structure in Mg-Zr-H system, prepared by GPa hydrogen pressure method, reveals reversible hydrogen storage up to ~ 3 wt.% [4].

In this work, ball milling in a reactive H2/D2 atmosphere was employed to explore the possibility of producing quaternary Mg and Ti-containing metal hydrides in Mg-Ti-Zr-H(D) system and to study possible Mg/Ti induced changes in their kinetic and thermodynamic properties.

The results for 0.45Mg: 0.30Ti : 0.25Zr elemental powder mixture ball milled in 50 bar of H2 (D2) were compared with those obtained for 4MgH2 : 2ZrH2 : TiH2 hydrides mixtures milled in 70 bar of H2. The changes in H2 (D2) pressure were monitor during milling. For Mg0.45Ti0.30Zr0.25 gas absorption was detected within the first 18 hours. No pressure change was observed during milling of the hydride mixture.

Powder X-ray and neutron diffraction analysis for the as-milled Mg0.45Ti0.30Zr0.25 showed the formation of a single FCC phase (a = 4.6524(5) Å) with a small fraction of ZrH1.9 and MgH2. If the obtained FCC corresponded to the ZrHx, it should release hydrogen at ~ 800 – 900 K. However, differential scanning calorimetry displayed only one desorption peak at 587 K, suggesting that Mg and/or Ti were present in the crystal structure of the synthesized compound. Results of thermogravimetric analysis revealed the desorption of ~ 2.0 wt.% of H2.

Powder X-ray diffraction data for the as-milled 4MgH2 : 2ZrH2 : TiH2 also showed the formation of the single FCC phase with a slightly larger cell parameter (a = 4.69912(5) Å) than the one observed for Mg0.45Ti0.30Zr0.25 – H(D) .

References

[1] R.A.H. Niessen, P.H.L. Notten, Electrochem. Solid. St. 8 (2005) A534
[2] W.P. Kalisvaart, P.H.L. Notten, J. Mater. Res. 8 (2008) 2179.
[3] S. Rousselot, M.-P. Bichat, D. Guay, L. Roue, J. Power Sources 175 (2008) 621.
[4] T. Takasaki, D. Kyoi, N. Kitamura, S. Tanase, T. Sakai J. Chem. B 111 (2007) 14102.

Microscopy and Microanalysis, July 29 – August 2, Phoenix, USA

Investigating the Spatial Distribution of Plasmon Modes in Carbon Cones

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Carbon cones (Figure 1a) have a unique topography which makes them promising for applications in hydrogen storage, sensors and electrodes [1]. Krishnan et al. showed that the hollow multiwalled carbon cones exhibit discrete apex angles of 112.9˚, 84.6˚, 60˚, 38.9˚ and 19.2˚, which corresponds to the incorporation of 1- 5 60˚ disclinations in a hexagonal graphitic sheet [2]. The cones investigated in this work have been produced from crude oil with a plasma arc. In addition to cones, samples contain a significant amount of flat carbon discs, which can be considered as cones with an apex angle of 180°. Determining the electronic structure of individual cones is of great interest for further understanding of carbon nanostructures as well as for potential future applications. Electron energy loss spectroscopy in the scanning transmission electron microscope (STEM- EELS) is an excellent technique for investigation of the electronic structure of the carbon cones, as it allows for investigation of individual particles both high spatial and energy resolution.

M. Kociak et al. [3] identified the orientation dependence of plasmon excitations in nanotubes and carbon onions by comparing the results of low loss EELS line scans with the corresponding High Angle Annular Dark Field (HAADF) image intensity profiles, and to semi- classical simulations of surface plasmon excitations in EEL spectra of carbon onions. They related specific plasmon modes to either the in-plane or out-of-plane component of the dielectric tensor [3]. In the present study, this approach has been extended to 2-D EELS spectrum images, in order to map the relative contribution and spatial distribution of plasmon modes for each of the cone geometries, at the tip area. An example is shown in Figure 1b where the spatial distribution of the surface excitation of σ electrons (associated with the σ-σ* transition) [3] is mapped for a cone with 2 pentagons at the tip (Figure 1a). Compared to the HAADF image (Figure 1a), the relative intensity of the 'σ-σ* mode' clearly peaks at the edge (i.e. the surface) of the cone (Figure 1b). The map was integrated over a 4eV window as indicated by the spectrum in Figure 1c. All data were acquired with the Nion UltraSTEM at 60kV to minimize irradiation damage, with an energy spread of 0.3eV. The spectra were deconvoluted for thickness and then de-noised using multivariate statistical analysis as implemented in the HREM Research MSA plug-in for Digital Micrograph [4].

References

[1] J. Muller et al., *Silicon Versus Carbon*, Y. Magarshak, S. Kozyrev, A.K. Vaseashta (ed), 2009 p.
285-292.
[2] A. Krishnan et al., *Nature*, **388** (1997) 451
[3] M. Kociak et al., *Phys. Rev. B*, **61** (2000) 13936

[4] M. Watanabe, et al., *Microsc. Microanal*, **13** (2007) 1264
[5] This work was supported by the Research Council of Norway under Contract No. 191621/V30

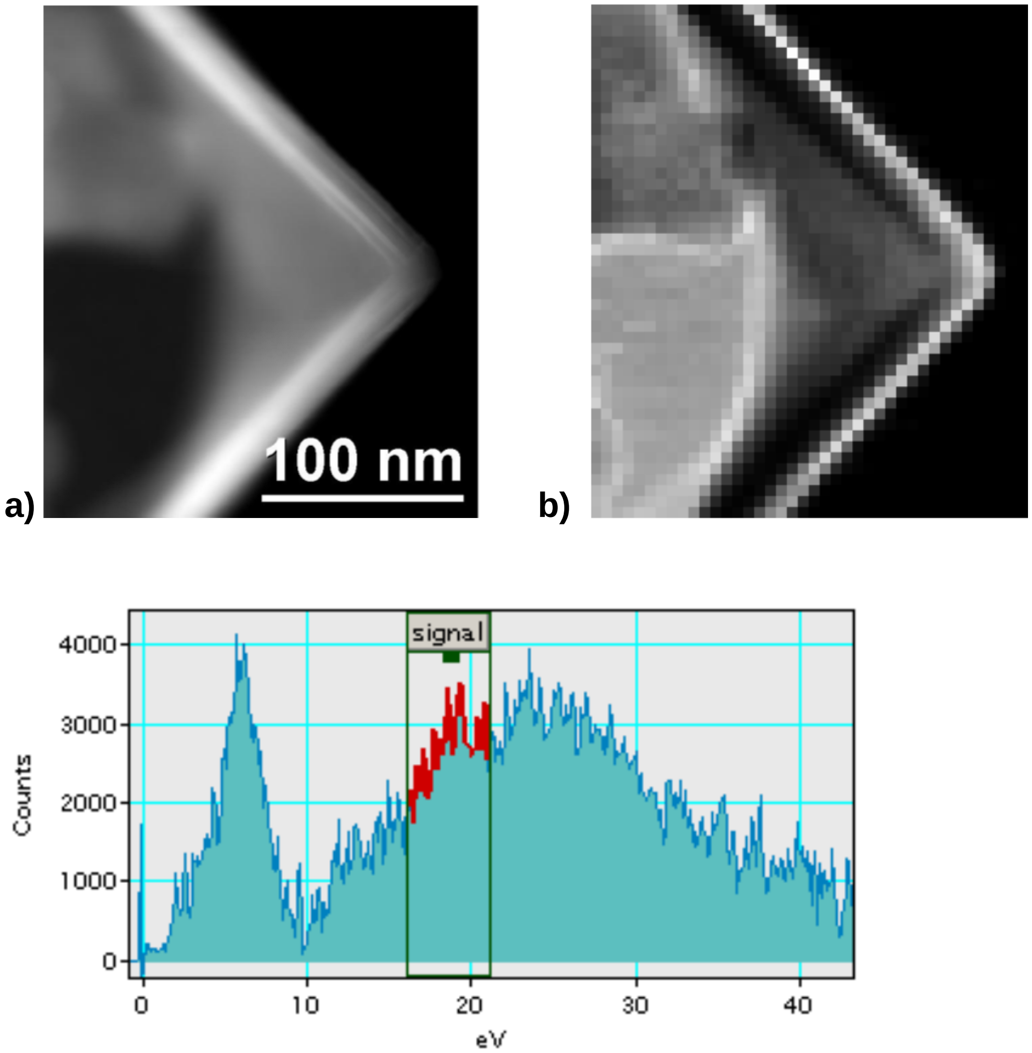

Figure. 1. (a) A HAADF image of a carbon cone. (b) The corresponding EELS- SI map showing the spatial dispersion of the ‘σ-σ*‘surface plasmon mode. The surface mode signal was integrated over a 4 eV window as indicated in the EELS spectrum in (c).

Neutrons Scattering for Studies of Materials – Activities at IFE in Norway

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Neutron scattering is a powerful method for investigation of the static and dynamic properties of materials. In particular neutrons are important: (i) for detailed studies of compounds with both light (e.g. hydrogen or oxygen) and more heavy elements, (ii) to determine magnetic structures and magnetic excitations, (iii) to distinguish atoms in compounds consisting of neighboring elements in the Period Table, (iv) to distinguish isotopes (e.g hydrogen and deuterium), and (v) to determine elementary excitations in matter. Furthermore, the weak interaction of neutrons with most elements results in determination of real bulk properties and easy use of complex sample environments. Diffraction with neutrons and X-rays are complementary methods, and both techniques are very often important for detailed studies of the structural properties.

The 2 MW JEEP II reactor at IFE, Kjeller is at present the only neutron source in the Nordic countries. On the other hand, the European Spallation Source, ESS, to be constructed in Lund in Sweden, will become the strongest neutron source in the world. IFE is already involved in ESS activities.

This talk will present the possibilities for neutron scattering experiments at the JEEP II reactor and with a main focus on our activities on characterization of hydrogen storage materials with powder neutron diffraction and small angle neutron scattering (SANS) techniques. The complementary use of synchrotron X-ray scattering, both powder diffraction and small-angle X-ray scattering (SAXS) will be described and emphasized.

Materials Science Summit, November 25 –December 1, Sendai, China

Structural Studies of Hydrogen Storage Materials

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One of the greatest technological barriers of widespread introduction of hydrogen in global energy systems is an efficient and safe storage method. Hydrogen chemically bonded in metals or intermetallic alloys constitutes a storage alternative where very high volumetric densities can be obtained. However, in the known materials for hydrogen storage, it is always a trade-off between volumetric densities, gravimetric densities, stability, kinetics, price and safety. During the last years new hydrogen storage materials with improved properties have been synthesized and characterized. In particular novel complex hydrides based on the elements aluminium, boron, magnesium and nitrogen have been extensively studied.

In order to understand the properties of materials and also to be able to determine new compounds, detailed knowledge about the position of the atoms is of major importance. Neutron diffraction is a unique tool for studies of hydrogen/deuterium in hydrogen storage materials. For studies of complex structures, compounds with both light and heavier elements, like H-containing compounds, and samples with more than one phase, the combination of powder neutron diffraction (PND) and X-rays diffraction (PXD) is crucial. For very complicated structural features and *in-situ* experiments, the use of synchrotron radiation X-rays (SR-PXD) is important.

Ball-milling at different conditions: in Ar, reactive milling with maximum 100 bar in H_2 and at liquid nitrogen temperature (cryomilling) has been used as the main synthesis method. The PND experiments are performed with the PUS diffractometer at the JEEP II reactor at IFE and the SR-PXD experiments at the Swiss-Norwegian Beam-lines (SNBL) at ESRF, both with the high-resolution setup and the MAR image plate system for in-situ experiments. Furthermore, IR, Raman and NMR methods have contributed to the understanding of structural features. The hydrogen storage properties have been studied with TG-DSC, mass spectroscopy, Thermal Programmed Desorption methods and Pressure-Composition Isotherm techniques.

Selected structural detailed structural studies and in-situ desorption diffraction experiments will be presented. In particular the presentation will address recent studies of novel boron- and magnesium-based hydrogen storage materials. The combination of SR-PXD and PND has in particular been important and will be emphasized.

Financial support from Research Council of Norway and European Commission FP6 and FP7 projects are acknowledged.

MH2012, October 21-26, Kyoto, Japan

Synthesis, Crystal Structure and Properties of Novel Borohydrides

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Borohydrides are attractive for hydrogen storage because of their high gravimetric hydrogen density. They suffer, however, from sluggish kinetics, high desorption temperatures and poor reversibility. One route to tailor the thermodynamics is by preparation of double-cation borohydrides: $M_xM_y'(BH_4)_n$. Another possibility for thermodynamics modification is anion substitution as demonstrated for $Na_3AlH_{6-x}F_x$ [1]. Recently halide-substituted borohydrides have been synthesized in the cases of $LiBH_4$-LiX (X=Cl, Br, I) [2], $Na(BH_4)_{1-x}Cl_x$ [3] and $Mg(BH_4)_{2(1-x)}Cl_{2x}$ [4]. Novel compounds can also be synthesized with both anion and cation substitution, for example $LiCe(BH_4)_3Cl$ [5].

Synthesis and characterization of transition metal and mixed borohydrides with anion and/or cation substitution will be presented. The presentation will include examples of novel binary borohydrides, novel compounds based on Li- or Na-borohydrides mixed with transition metals or rare-earth chorides and anion substitution in borohydrides. The compounds have been synthesized by mechano-chemical reactions (ball-milling) between an alkali/alkaline earth borohydride and a different metal chloride. This method allows the synthesis of unsolvated compounds that have not been obtained by alternative chemical methods. Recently we have found new solvent-free rare-earth borohydrides based on Ce, Tb, Er and Yb.

The structural and hydrogen storage properties have been investigated by powder neutron and X-ray diffraction including the use of synchrotron radiation X-rays at SNBL at ESRF, IR and Raman spectroscopy, DSC, TG-DSC-MS and Temperature Programmed Desorption.

The work has been funded by the Research Council of Norway and EU-projects FLYHY, Marie-Curie project MaterHy and SSH2S.

References

[1] H.W. Brinks, A. Fossdal, B.C. Hauback, J. Phys. Chem. C 112 (2008) 5658.

[2] L. Mosegaard, B. Møller, J.-E. Jørgensen, Y. Filinchuk, Y. Cerenius, J.C. Hanson, E. Dimasi, F. Besenbacher, T.R. Jensen, J. Phys. Chem. C 112 (2008) 1299; L.H. Rude, O. Zavorotynska, L.M. Arnbjerg, D.B. Ravnsbæk, R.A. Malmkjær, H. Grove, B.C. Hauback, M. Baricco, Y. Filinchuk, F. Besenbacher, T.R. Jensen, Int. J. Hydrogen Energy 36 (2011) 15664.

[3] J.E. Olsen, M.H. Sørby, B.C. Hauback, J. Alloys Compd. 509 (2011) L228; I. Llamas-Jansa, N. Aliouane, S. Deledda, J.E. Fonneløp, C. Frommen, T. Humphries, K. Lieutenant, S. Sartori, M.H. Sørby, B.C. Hauback, J. Alloys Compd. 530 (2012) 186.

[4] S. Hino, J.E. Fonneløp, M. Corno, O. Zavorotynska, A. Damin, B. Richter, M. Baricco, T.R. Jensen, M.H. Sørby, B.C. Hauback, J. Phys. Chem. C (2012) in press.

[5] C. Frommen, M.H. Sørby, P. Ravindran, P. Vajeeston, H. Fjellvåg, B.C. Hauback, J. Phys. Chem. C 115 (2011) 23591.

WHEC 2012, June 3-7, Toronto, Canada

TASK 22 of IEA HIA – Fundamental and Applied Hydrogen Storage Materials Development

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An effective method for storage of hydrogen is a technological challenging aspect of achieving a hydrogen-based economy. Hydrogen storage in solid materials is the only method that can fulfill international long-term goals for the use of hydrogen in vehicles with respect to both gravimetric and volumetric hydrogen density. At present no materials satisfy the goals, but during the last years a number of promising materials have developed.

Task 22 "Fundamental and Applied Hydrogen Storage Materials Development" in the IEA HIA is the largets international collaborative effort in the field of hydrogen storage with 54 Experts from 17 countries. Task 22 has the following targets:

A. Develop a reversible or regenerative hydrogen storage medium fulfilling international targets for hydrogen storage.
B. Develop the fundamental and engineering understanding of hydrogen storage by various hydrogen storage media that have the capability of meeting Target A.
C. Develop hydrogen storage materials and systems for use in stationary applications. Task 22 is open to reversible metal hydrides, regenerative hydrogen storage materials and nanoporous materials.

The presentation will address challenges with respect to hydrogen storage and give and overview of the present status of hydrogen storage materials development using ecamples from the Task 22 collaboration.

Synthesis and Characterisation of Novel Borohydrides

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Due to the high gravimetric and volumetric hydrogen densities, metal borohydrides M(BH4)n are among the most attractive candidates as hydrogen storage materials. However, the practical applications are limited by high thermodynamic stability, e.g. LiBH4 and NaBH4 or the reaction kinetics in for example Mg(BH4)2 and Ca(Bh4)2. A major challenge is reversibility at moderate conditions. Double-cation borohydrides MxM`y(BH4)n is a possible route to tailor the thermodynamics. Another possibility is anion substitution as shown for the Na-alanate in Na3AlH6-xFx, LiBH4-LiX with X-Cl, Br, I, and recently Na(BH4)1-xClx. Furthermore, both anion and cation substitution has been reported for KZn(BH4)Cl2 and recently for LiCe(BH4)3Cl.

Synhesis and characterization of novel transition metal and mixed borohydrides with anion and/or cation substitution will be presented. The presentation will include examples of novel binary borohydrides, novel compounds based on Li- or Na-borohydrides mixed with transition metals or rare-earth elements and anion substitution borohydrides. The compounds have been synthesized by ball-millimg techniques. Their structural and hydrogen storga eproperties have been investigated by neutron and X-ray diffraction including synchrotron radiation X-rays, IR and Raman spectroscopy, NMR, DSC, TG-DSC-MS and Temperature Programmed Desorption.

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MarchCOMeeting'12, March 6-9, Havanna, Cuba

Field Induced Microparticle Structure Formation in Fluids

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We review how magnetic and electric fields can be used to create microparticle structures within fluids such as water, oil, polymers or ferrofluids. The particular arrangement of the electrodes will strongly influence the morphology of the clusters or networks formed, as will also rotating or oscillating fields do. The dynamics of such pattern formation will be described for various types of particles, such as colloidal microspheres, carbon nanoparticles and metal particles.

“MHS – Future Perspectives ?”, June 14-18, Norwegian Coastal Express

Synthesis of New Complex Hydrides in Liquid Ammonia

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Metal aluminum amides $M[Al(NH_2)_4]_x$ store hydrogen in the form of amide $[NH_2]^-$, and release ammonia upon heating at around 100 °C [1]. Creation of composites with metal hydrides enables replacement of ammonia release by hydrogen. For instance, the composite of $LiAl(NH_2)_4$ and LiH desorbs more than 5 mass% hydrogen below 130 °C [2]. Metal aluminum amide can be synthesized by reaction of alkali metal hydride and Al with liquid ammonia [1, 3]. In this study, synthesis of analogous compound $M[B(NH_2)_4]_x$ has been tried. Metal borohydrides and metal hydrides + ammonia borane were milled in liquid ammonia. Structure and gas desorption properties of the milled materials were investigated with powder X-ray diffraction (XRD) and thermogravimetry-mass spectroscopy combined analysis, respectively.

$LiBH_4$ milled under liquid ammonia transformed into ammoniate $LiBH_4$ nNH_3. XRD measurement exhibits the mixture of LiH and B milled under liquid ammonia contains $LiNH_2$ and unreacted B. XRD pattern of the mixture of MgH_2 and ammonia borane milled under liquid ammonia shows unknown profile and it does not match with magnesium amidoborane ammoniate [4]. The mixture after milling desorbs hydrogen and ammonia at around 100 °C. Structure solution of this compound is in progress.

[1] T. Ono, et al, *J. Alloys Compd.*, **506** (2010) 297-301.
[2] R. Janot, J. Eymery, J. Tarascon, *J. Phys. Chem. C*, **111** (2007) 2335–2340.
[3] P.P. Molinie, R. Brec, J. Rouxel, P. Herpin, *Acta Cryst.* **B29** (1973) 925–932.
[4] Y.S. Chua, et al, Chem. Commun., **46** (2010) 5752-5754.

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High Pressure NMR Studies of Complex Hydrides

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The hydrogenation pathway of complex hydrides has been highly debated in recent years. The foremost reason for this is the dearth of analytical techniques available to characterize the intermediates synthesized during the hydrogenation process. In-situ powder X-ray diffraction studies have proven dominant in recent years due to the high sensitivity and the possibility to identify and quantify distinct phases and solve structures of the unknown. In-situ NMR spectroscopy has proven valuable for the identification of the dehydrogenation pathway of many hydrides1,2 but the inability to pressurize samples under H2 during experiments has inhibited this technique for hydrogenation reactions.

The in-situ hydrogenation of decomposed NaAlH4 (1) and LiAlH4 (2) has been studied using a High Pressure NMR Cell. The hydrogenation of NaAlH4 has been studied by 27Al and 23Na wide line NMR spectroscopy, while 7Li and 27Al was studied for LiAlH4. The hydrogenation study of decomposed NaAlH4 was the most intriguing. It has been suggested previously that the formation of NaAlH4 is not observed until the formation of Na3AlH4 is at a maximum.3 Fig. 1 depicts the evolution of a peak corresponding to Na3AlH4 followed by the insurgence of NaAlH4 after 4 only mins. The in-situ hydrogenation of LiAlH4 has not been measured previously due to the fact that the reaction takes place as a slurry. NMR spectroscopy is perfect for these measurements and illustrates the synthesis reported previously by Ashby4 and Graetz.5 As predicted, LiAlH4 is formed without a preceding hexahydride intermediate to form the solvated tetrahydride.

$$\mathrm{NaH + Al} \xrightarrow[\text{2mol\% TiCl}_3]{\text{140 bar H}_2\text{, 120°C}} \mathrm{NaAlH_4} \qquad (1)$$

$$\mathrm{LiH + Al} \xrightarrow[\text{THF, 0.5mol\% TiCl}_3]{\text{35 bar H}_2\text{, 40°C}} \mathrm{LiAlH_4{\cdot}4THF} \qquad (2)$$

This study highlights the importance of NMR spectroscopy as a valuable tool in the characterization and understanding of the processes involved during reversible hydrogenation. The hydrogenation pathway of TiCl3 doped NaAlH4 and LiAlH4 are now more clearly defined.

References

(1) Verkuijlen, M. H. W.; van Bentum, P. J. M.; Zabara, O.; Fichtner, M.; Kentgens, A. P. M. *J. Phys. Chem. C* **2011**, *115*, 13100. (2) Wiench, J. W.; Balema, V. P.; Pecharsky, V. K.; Pruski, M. *J. Solid State Chem.* **2004**, *177*, 648. (3) Walters, R. T.; Scogin, J. H. *J. Alloy. Compd.* **2004**, *379*, 135. (4) Ashby, E. C.; Redman, H. E.; Brendel, G. J. *Inorg. Chem.* **1963**, *2*, 499. (5) Graetz, J.; Wegrzyn, J.; Reilly, J. J. *J. Am. Chem. Soc.* **2008**, *130*, 17790.

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A new Polymer and it'sTemperature-induced Transitions

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In order to elucidate the interplay between hydrophobic and hydrophilic forces as well as electrostatic interactions for a polymer in an aqueous environment, we have designed a novel pentablock polymer, with the configuration ABCBA. This is a linear chain, where we have attached two hydrophobic blocks (B) to each side of a hydrophilic segment (C), and on the end of the chain we have attached negatively charged groups (A). In this system there will be a competition between the attractive force of the hydrophobic blocks, the repulsion between the charged groups, and the tendency for the hydrophilic group to maximize the interaction with the surrounding water. The polymer has been made in two versions, with different lengths of the hydrophilic block (C), having 34 and 77 C-atoms, respectively. We observe that the physical properties of the system are highly dependent on the length of this C block. A sharp and highly reproducible temperature-induced transition, related to changes in chain conformation, is observed at a temperature around 40 C. The reason for this behavior, as well as the final structures produced in this system will be discussed in the presentation.

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Anisotropy in PS-clay Nanocomposites

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Recent progress in polymer science has demonstrated that remarkable changes in material properties are achievable by combining polymer systems with miniature particles, where at least one of the particle dimensions is in the nanosize range. Important examples are large increases in melting temperature as well as significantly higher yield stress. Less than 1 wt.% filler can drastically modify the overall system behavior if the surface of the incorporated particles has been made to interact sufficiently with the polymer chains[1].

We have developed a new method of synthesizing polystyrene-clay nanocomposites, where the clay particles are manipulated into chains spanning the whole polymer volume. Synthesis, structure determination, and physical properties of the composites will be discussed.

[1] Haraguchi, K. and T. Takehisa, *Advanced Materials*, 2002. **14**(16): p. 1120-1124.

Synthesis and Characterisation of Polystyrene-Clay Nanocomposites

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Recent progress in polymer science has demonstrated that remarkable changes in material properties are achievable by combining polymer systems with miniature particles, where at least one of the particle dimensions is in the nanosize range. Even minute quantities (sometimes less than 1 5) can drastically modify the overall system behavior if the surface of the incorporated particles has been made to interact sufficiently with the polymer chains. Fu et al [1] dispersed organically modified montmorillonite clay into polystyrene (PS), and increased the dynamic modulus of the nanocomposite by over 60 %, with only 8 wt-% filler material. We recently started to build upon Fu et al's work on PS-clay systems, by incorporating other types of smectic clays, such as Laponite and Fluorohectorite, and also manipulating the orientation and super structure of the clay particles with electric fields. The presentation will give a brief summary of the synthesis and characterization of such composites.

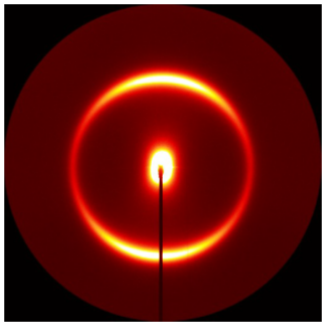

Figure 1: SAXS scattering pattern of PS-fluorohectorite composite.

[1] X. Fu and S. Qutubuddin, Materials Letters 42 (2000) 12.

"MHS - Future Perspectives ?", June 14-18, Norwegian Coastal Express

Structure and decomposition study of Yb-containing borohydrides

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Hydrogen can act as an energy carrier and substitute fossil fuels in both stationary and mobile applications. Ongoing research shows that metal borohydrides can store hydrogen in a safe and efficient way, with high gravimetric hydrogen densities and volumetric densities significantly exceeding those in compressed gas or liquid hydrogen. However, most of the light metal borohydrides are thermodynamically too stable for storage applications.

Recently transition metal and rare-earth metal borohydrides have been synthesized by mixing the respective metal chloride with a simple alkali metal borohydride [1-3]. Here we present the results for the ytterbium chloride – lithium borohydride system.

Mechanochemical processing of $YbCl_3$ with $LiBH_4$ results in three new ytterbium-containing phases. Short reaction time results in the formation of $LiYb(BH_4)_4$ with lattice constants a = 6.16 Å and c = 12.3Å. It crystallizes in the tetragonal space group *P-42c*. The structure contains tetrahedral $[Yb(BH_4)_4]$- complex anions, similar to those reported for $LiSc(BH_4)_4$ [4]. Longer milling time promotes the crystallization of $Yb(BH_4)_3$. There are two $Yb(BH_4)_3$-modifications, α-$Yb(BH_4)_3$ which crystallizes in the space group *Pa-3* (a≈10.75 Å), and metastable β-$Yb(BH_4)_3$ (space group *Fm-3c,* (a≈10.9 Å). Both structures have been determined from high-resolution synchrotron radiation powder X-ray diffraction (HR SR-PXD) data obtained at the Swiss-Norwegian beam line (SNBL) of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. In addition, the decomposition path of this mixture has been studied using in situ SR-PXD at SNBL. Both the structures of these phases and their decomposition routes will be presented at the meeting.

1. Frommen, C., et al., *Crystal structure, polymorphism, and thermal properties of yttrium borohydride Y(BH(4))(3).* Journal of Alloys and Compounds, 2010. **496**(1-2): p. 710-716.
2. Frommen, C., et al., *Synthesis, Crystal Structure, and Thermal Properties of the First Mixed-Metal and Anion-Substituted Rare Earth Borohydride LiCe(BH4)3Cl.* The Journal of Physical Chemistry C, 2011. **115**(47): p. 23591-23602.
3. Rude, L.H., et al., *Tailoring properties of borohydrides for hydrogen storage: A review.* Physica Status Solidi a-Applications and Materials Science, 2011. **208**(8): p. 1754-1773.
4. Hagemann, H., et al., *LiSc(BH4)(4): A novel salt of Li+ and discrete Sc(BH4)(4)(-) complex anions.* Journal of Physical Chemistry A, 2008. **112**(33): p. 7551-7555.

Reversibility in $Ca(BH_4)_2$

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$Ca(BH_4)_2$ is considered a promising material for hydrogen storage applications due to its high gravimetric and volumetric capacity as well as predicted thermodynamic properties suitable for hydrogen storage purposes. However, the material displays poor reversibility. Previous studies on the reversibility of $Ca(BH_4)_2$ have shown up to 60% rehydrogenation at high temperature/high pressure conditions when starting from CaB_6 + CaH_2, and at more moderate conditions from decomposed $Ca(BH_4)_2$ when catalysts are added.[1,2] However, the details of the rehydrogenation mechanism, including knowledge about the phases present in the desorbed state and the role of the additive are not known.

In the work presented here the rehydrogenation properties of $Ca(BH_4)_2$ decomposed at two different temperatures (320 and 340 °C) were investigated. The dehydrogenated samples were exposed to a hydrogen pressure of 100 bar at 305 °C, and the dehydrogenated and rehydrogenated samples were characterized by powder X-ray diffraction (PXD) and infrared (IR) spectroscopy. Quantitative PXD analysis shows that up to 29 % $Ca(BH_4)_2$ is formed after rehydrogenation without addition of a catalyst. The results further show a correspondence between rehydrogenation properties and decomposition temperature. Bragg peaks from the intermediate CaB_2H_x[3]are not present after rehydrogenation, suggesting complete rehydrogenation of this phase at the given conditions. This corresponds to a recent result reported by Kim et al.[4] However, decomposition of CaB_2H_x due to a reaction with phases formed during rehydrogenation of the amorphous phase(s) cannot be excluded, and further investigations are thus required.

Modes from unidentified amorphous phases are observed in the IR spectra, implying that decomposition products different from the expected phases are formed during de/re-hydrogenation. Due to lack of literature spectra matching the observed ones, no further insight to the composition of these phases can at present be obtained.

[1] Ronnebro, E.; Majzoub, E. H. *Journal of Physical Chemistry B* **2007**, *111*, 12045.
[2] Kim, J. H.; Shim, J. H.; Cho, Y. W. *J. Power Sources* **2008**, *181*, 140.
[3] Riktor, M. D.; Sorby, M. H.; Chlopek, K.; Fichtner, M.; Hauback, B. C. *Journal of Materials Chemistry* **2009**, *19*, 2754.
[4] Kim, Y.; Hwang S. J.; Shim, J. H.; Lee, Y. S.; Han, H. N.; Cho, Y. W. *Journal of Physical Chemistry C* **2012**, *116*, 4330.

“MHS - Future Perspectives ?”, June 14-18, Norwegian Coastal Express

Influence of transition metal oxides on $Mg(BH_4)_2$ decomposition

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Magnesium borohydride is one of the most perspective hydrogen storage material thought its kinetics and reversibility are the main challenges. Decomposition of $Mg(BH_4)_2$ occurs via several stages [1-4]. Depends on the conditions different magnesium polyboranes may exist during the reaction. One of the most stable intermediate is dodecaboranate that eventually transformed to MgB_2. Geometrical similarity of boron icosahedral frame-work in $MgB_{12}H_{12}$ and bulk boron can be a reason of kinetic stability of the dodecaboranate [5] that hampers formation of $Mg(BH_4)_2$. Apparently partially rehydrogenation of $Mg(BH_4)_2$ from lower polyborane might be possible at reasonable hydrogen pressure and temperature [6]. A catalyst that favors to avoid dodecaboranate formation may be one of the possibilities to improve the reversibility and kinetics of $Mg(BH_4)_2$ decomposition. High valence transition metal compounds where anion is oxygen, carbon or halogens have ability to form hydrogen bonds with different stoichiometry providing fast dissociation to atomic hydrogen or its recombination to hydrogen molecules [7]. An optimum stability of the transition metal compounds can be found for some oxides which are less stable than their corresponding halogenides but not consumed by the hydrogenation/dehydrogenation themself. Some transition metals oxides were checked as possible catalysts for $Mg(BH_4)_2$ decomposition. Catalyst screening and detailed optimization based on TiO_2 and MoO_3 additives are presented in this work. It was suggested that approximately 30°C decrease of $Mg(BH_4)_2$ temperature decomposition might be the result of increased entropy factor [8].

[1] G. Soloveichik, Y. Gao, J. Rijssenbeek, M. Andrus, S. Kniajanski, R. C. Bowman, Jr, S. J. Hwang, J. C. Zhao. *J. Hydrogen Energy* 34 (2009) 916-928.
[2] H. W. Li, K. Kikuchi, Y. Nakamori, N. Ohba, K. Miwa, S. Towata, S. Orimo. *Acta Materialia* 56 (2008) 1342-1347.
[3] K. Chłopek, C. Frommen, A. Léon, O. Zabara, M. Fichtner. *J. Mater. Chem.* 17 (2007) 3496-3503.
[4] E. Rönnebro. *Cur. Op. S. St. Mater. Sci.* 15 (2011) 44-51.
[5] H. W. Li, K. Miwa, N. Ohba, T. Fujita, T. Sato, Y. Yan, S. Towata, M. W. Chen, S. Orimo. *Nanotechnology* 20 (2009) 204013-204020.
[6] M. Chong, A. Karkamkar, T. Autrey, S. Orimo, S. Jalisatgi, C. M. Jensen. *Chem. Commun.* 47 (2011) 1330-1332.
[7] G. Barkhordarian, T. Klassen, R. Bormann. *J. Chem. Phys. B* 110 (2006) 11020-11024.
[8] M. Fichtner. *Nanotechnology* 20 (2009) 204009-204013.

Desorption and Morphology of Nano-confined $Li^{11}BD_4$-$Mg(^{11}BD_4)_2$

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Light element and complex anion hydrides, for example MgH_2, $MAlH_4$ (M=Li, Na, K) and especially light metal borohydrides such as $Mg(BH_4)_2$ and $LiBH_4$, are attractive storage materials for vehicular applications because of their high gravimetric and volumetric hydrogen capacities. Recently, a physical mixture of metal borohydrides, $LiBH_4$-$Mg(BH_4)_2$, has been proposed as a hydrogen storage material [1]. The 1:1 mixture exhibited a eutectic melting at 180 ^{o}C and a decomposition temperature much lower than those of the pure borohydrides.

In the present work we investigated the effect of nano-confinement on the desorption and morphological behaviour of this borohydride mixture, in the form of double labelled variant $Li^{11}BD_4$-$Mg(^{11}BD_4)_2$, where hydrogen has been substituted by deuterium and natural boron by ^{11}B in order to optimize the neutron scattering studies on this type of materials [2-4].

The nano-confined mixture has been compared to the corresponding mixture in the bulk form. The systems were investigated by several techniques: small-angle neutron scattering and ^{11}B nuclear magnetic resonance, among others. The dehydrogenation temperatures decreased by up to 60 ^{o}C in the nano-confined system. Most importantly, desorption from the nano-confined hydride proceeds without formation of diborane, B_2D_6, which evolves from the bulk mixture. From small-angle neutron scattering, differences in morphology between the bulk and the nano-confined systems are also demonstrated. Furthermore, ^{11}B NMR data show that nano-confinement inhibits the formation of dodecaborane, $[B_{12}D_{12}]^{2-}$, during decomposition.

[1] Bardaji E G, Zhao-Karger Z, Boucharat N, Nale A, van Setten M J, Lohstroh W, Roehm E, Catti M and Fichtner M 2011 *J. Phys. Chem. C* **115** 6095
[2] Sartori S, Knudsen K K, Zhao-Karger Z, Bardaji E G, Fichtner M and Hauback B C 2009 *Nanotechnology* **20** 505702
[3] Sartori S, Knudsen K K, Zhao-Karger Z, Bardaji E G, Muller J, Fichtner M and Hauback B C 2010 *J. Phys. Chem. C* **114** 18785
[4] Sartori S, Knudsen K K, Roth A, Fichtner M and Hauback B C 2012 *Nanoscience and Nanotechnology Letters* **4** 173

MCARE2012, February 26 –March 1, Clearwater, Florida, USA

Influence of Carbon Nanostructures on Metal Hydrides for Hydrogen Storage Applications

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The synthesis of nano-sized particles infiltrated in carbon structures has being investigated as an alternative way to improve the properties of metal hydrides for hydrogen storage applications. The kinetics of this type of materials has been found to be significantly improved but the possible change in thermodynamics is still not clear. The successful wet or melt infiltration of nanoparticles of $Mg(BH_4)_2$, $NaAlH_4$ and MgH_2 into carbon fibers and activated carbons have been demonstrated by small-angle neutron scattering (SANS) performed at the JEEP II reactor at IFE. With the complementary *in situ* small-angle X-ray scattering (SAXS), it has been possible to underline important differences in the morphology and surface area of the hydride particles when they are nano-confined in the porous scaffolds, compared to their values in the bulk state.

In this talk the latest work concerning SANS, SAXS and wide-angle X-ray scattering investigations of several hydrides will be presented. TEM, NMR and desorption data will contribute in some cases to clarify the properties of the nano-composites. The interaction of the hydrides with the carbon structures will also be taken into account.

NANO2012, August 26-31, Rhodes, Greece

Nanoconfinement Effects in a Mixed Lithium-Magnesium Borohydride System for Hydrogen Storage

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Within the field of hydrogen storage materials for vehicular applications there are several challenges to be addressed. In general these materials, such as complex and binary metal hydrides, offer a high theoretical hydrogen storage content but their thermodynamics and kinetics are not suitable for reversibility at moderate conditions. During the last years some improvements have been obtained with the addition of dopants or through solid state reaction systems but the results are still far from the car industry requirements.

An alternative method explored recently is the preparation of nanoconfined systems where the H storage materials are infiltrated in nanoporous scaffolds. The rational behind these experiments is that size and interface effects in the systems could alter both kinetics and thermodynamics of the hydrides.

The nanoconfined materials investigated so far showed different properties when compared to the bulk. In most cases the kinetics was enhanced while the thermodynamic modification could be achieved only when the particles sizes were at the lower nanometer range, and towards destabilization or stabilization, depending on the system. In the case of nanoconfined MgH_2, $Mg(BH_4)_2$ and $NaAlH_4$, small-angle neutron scattering (SANS) performed at the JEEP II reactor, at IFE, proved the effective confinement of the hydrides with particle sizes ranging from around 1 to 6 nm, depending on the scaffold and/or the material.

In this talk the influence of nanoconfinement on the properties of a mixture of lithium-magnesium borohydride, $Li^{11}BD_4$-$Mg(^{11}BD_4)_2$, will be presented. The samples were investigated by thermal analysis, SANS, ^{11}B nuclear magnetic resonance and transmission electron microscopy.

The system presents a dehydrogenation temperature decreased by up to 60 ^{o}C and different gas evolution steps compared to the bulk material.

Most importantly, the nanoconfinement inhibits the evolution of toxic diborane, B_2D_6, and the formation of dodecaborane, $[B_{12}D_{12}]^{2-}$ during decomposition, two results which are promising for practical applications.

Collaboration with the group of Maximilian Fichtner at Karlsruhe Institute of Technology (KIT), Germany, under the EU project NANOHy ("Novel Nanocomposites for Hydrogen Storage Applications", contract n. 210092) is gratefully acknowledged.

SAS2012, November 18-23, Sydney, Australia

The role of Small-Angle Scattering on Nano-confined Hydrides for Hydrogen Storage

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One of the most promising routes towards a hydrogen economy is the use of hydrogen as energy vector for vehicular and stationary applications in the form of solid storage materials, such as hydrides. Practical utilization of these compounds is challenging because of their slow kinetics and high thermodynamic stability and thus far none of the studied materials satisfactorily meets the targets set by the U.S. Department of Energy

During the last years much emphasis has been placed on the synthesis of nanosized particles as an alternative way to improve the properties of the hydrides. Due to the characteristics of these nano-confined composites, powder X-ray and neutron diffraction were not useful in analyzing the data and some doubts were raised concerning the effective inclusion of the hydrides inside the pores of the scaffolds.

IFE has nearly 60 years of experience in the field of neutron scattering on hydrides due to its advanced neutron scattering instrumentation at the JEEP II reactor (high-resolution powder neutron diffractometer and small-angle neutron scattering, SANS). We therefore proposed the use of small-angle scattering as a method to investigate the new class of nano-confined hydrogen storage materials.

We demonstrated via SANS the successful wet or melt infiltration of $Mg(^{11}BD_4)_2$, $NaAlD_4$ and MgD_2 into nano-carbon templates.[1-3] Depending on the hydride and/or the scaffold used, the particle sizes were found to range from 1 to 6 nm. Combining SANS and *in situ* small-angle X-ray scattering (SAXS, performed at ESRF, Grenoble), it was possible to underline important differences in the morphology and surface area of the hydride particles during heating when they are confined in the nano-porous scaffolds, compared to their values in the bulk state.

We will present the latest work concerning SANS investigations on a mixture of $Li^{11}BD_4$-$Mg(^{11}BD_4)_2$ infiltrated in a carbon scaffold. The system results to be particularly interesting for hydrogen storage applications because the nano-confinement inhibits the formation of the undesirable dodecaborane $[B_{12}D_{12}]^{2-}$ and the evolution of B_2D_6 while improving the hydrides kinetics.

References

1) Sartori, S.; Knudsen, K.D., Zhao-Karger, Z., Gil Bardaji, E., Fichtner, M., and Hauback B.C et al. Nanotechnology, 20, 2009, 505702-505709.
2) Sartori, S.; Knudsen, K.D., Zhao-Karger, Z., Gil Bardaji, E., Muller, J., Fichtner, M., and Hauback B.C. Journal of Physical Chemistry C, 114, 2010, 18785-18789.
3) Sartori, S.; Knudsen, K.D., Roth, A., Fichtner, M., and Hauback B.C. Nanoscience and Nanotechnology Letters, 4, 2012, 173-177.

Weizmann Institute, December 7, Israel

Neutrons Scattering for Materials Research: Some Exciting Challenges in the Field of Hydrogen Storage for Vehicular Applications

Sabrina Sartori

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Knowing the structure of a system is essential to achieve the desired properties of the material. X-rays are scattered by the electrons surrounding the nucleus of an atom. As a result, heavy atoms with many electrons scatter x-rays more efficiently than light atoms (such as oxygen or, worse, hydrogen).

Unlike x-ray scattering, neutron scattering lengths do not increase linearly with atomic number. Instead they vary erratically, not only from element to element but from isotope to isotope. Therefore combining data from neutron and x-ray diffraction is the only way to resolve ambiguities in the crystal structure of various materials. Furthermore, small-angle neutron scattering is an invaluable tool to study nanostructured materials, disordered, porous and fractal structures, particle size distributions and interfaces/surface effects.

IFE has nearly 60 years of experience in the field of neutron scattering on hydrides due to its advanced neutron scattering instrumentation at the JEEP II reactor (mainly for high-resolution powder neutron diffraction and small-angle neutron scattering).

In this lecture we will present the basic principles of neutron scattering and the contribution of the Physics Department to investigate new class of materials for hydrogen storage applications.

Complex Workshop, January 30 – February 5, Porto de Galinhas, Brasil

CO_2 and Porous Media - SANS

Pawel A. Sobas[1], Kenneth D. Knudsen[1], Geir Helgesen[1], Arne Skjeltorp[1], Jon Otto Fossum[2]

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We are presently involved in research activities focusing on physical processes that are important for the understanding of CO_2 transport and storage into the ground. The relevant geological structures may show large variations in composition (water saturated porous materials, such as sandstone in a sedimentary basin, caprock, clays). CO_2 trapped in such porous materials relies on different mechanisms of confinement that act on different time scales. Some important factors to consider are: 1) an impermeable caprock that keeps the fluid underground (supercritical CO_2 fluid), 2) the solubility of the CO_2 in the water, 3) intercalation (absorption) into clay nanopores, 4) chemical reactions that bind the carbon in mineral form to the rock.

Small Angle Neutron Scattering (SANS) is a technique highly valuable for studying nanostructures (1-100nm), such as clays nanoparticl*es*, and this technique is available at Institute for Energy Technology (IFE). For the investigations on CO2 and porous materials we will make use of a specially designed cell to be used in combination with SANS. The cell allows studying nanoporous materials together with CO_2 in the supercritical state, up to 150°C and CO_2 pressure up to 690 bars. A specially adapted setup has now been made in order to integrate this CO_2 cell into the SANS apparatus. In addition, the instrument has been upgraded by the implementation of a new element - a so-called bender. This is designed to deflect neutrons with wavelengths above 4.5 Å by a certain amount (4°), thus removing fast neutrons and gamma radiation, in order to improve the quality of the neutron beam.

Hydrogen Storage Materials and Neutron Scattering at IFE – Present and Future

Magnus H. Sørby[1], Christoph Frommen[1], Sabrina Sartori[1], Marit Riktor[1] and Bjørn C. Hauback[1]

[1]*Institute for Energy Technology, Physics Department, 2027 Kjeller, Norway*

Effective hydrogen storage needs to be realized if hydrogen should be widely used as an energy carrier. Hydrogen storage in solids is the only solution that can yield energy densities comparable to fossil fuels.

The Physics department at IFE has a broad activity on hydrogen storage materials, including synthesis of new materials, structure determination and investigations of hydrogen sorption properties. The" in-house" availability of neutrons from the JEEP II reactor is a particular benefit for structural characterization due to the weak X-ray scattering of hydrogen.

The talk will give examples of recent research on structural characterization of hydrogen storage materials on the atomic and nanoscopic level using powder neutron diffraction and small angle neutron scattering, respectively. Emphasis will be on "borohydrides" which is a material class that shows very attractive gravimetric and volumetric hydrogen densities.

Future experimental possibilities, including the new powder diffractometer ODIN and beam lines for testing of ESS components, will also be presented.

EPDIC13, October 28-31, Grenoble, France

Hydrogen Storage and Energy Related Materials

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One of the greatest technological barriers of widespread introduction of hydrogen in global energy systems is an efficient and safe storage method. Hydrogen chemically bonded in metals or intermetallic alloys constitutes a storage alternative where very high volumetric densities can be obtained. However, in the known materials for hydrogen storage, it is always a trade-off between volumetric densities, gravimetric densities, stability, kinetics, price and safety. During the last years new hydrogen storage materials with improved properties have been synthesized and characterized. In particular novel complex hydrides based on the elements aluminium, boron, magnesium and nitrogen have been extensively studied.

In order to understand the properties of materials and also to be able to predict new compounds, detailed knowledge about the atomic structure is of major importance. Neutron diffraction is a unique tool for studies of hydrogen/deuterium-containing materials. For studies of complex structures, compounds with both light and heavier elements, like H-containing compounds, and multi-phase samples, the combination of powder neutron diffraction (PND) and X-rays diffraction (PXD) is crucial. For very complicated structural features and in-situ experiments, the use of synchrotron radiation X-rays (SR-PXD) is important.

Ball-milling at different conditions: in Ar, reactive milling with maximum 100 bar in H_2 and at liquid nitrogen temperature (cryomilling) has been used as the main synthesis method. The PND experiments are performed with the PUS diffractometer at the JEEP II reactor at IFE and the SR-PXD experiments at the Swiss-Norwegian Beam-lines (SNBL) at ESRF, both with the high-resolution setup and the MAR image plate system for in-situ experiments. Furthermore, IR, Raman and NMR methods have contributed to the understanding of structural features. The hydrogen storage properties have been studied with TG-DSC, mass spectroscopy, Thermal Programmed Desorption methods and Pressure-Composition Isotherm techniques.

Selected structural detailed structural studies and in-situ desorption diffraction experiments will be presented. In particular the presentation will address recent studies of novel boron- and magnesium-based hydrogen storage materials. The combination of SR-PXD and PND has in particular been important and will be emphasized.

Keywords: hydrogen storage, structure determination, in-situ studies

Halide Substitution in Borohydrides

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Alkali and alkaline earth metal borohydrides have been investigated as some of the most promising hydrogen storage materials for mobile use because of their high gravimetric hydrogen capacity. Among them, $Mg(BH_4)_2$ and $Ca(BH_4)_2$ contain large amount of hydrogen of 14.9 and 11.6 mass %, respectively, and it is predicted that these compounds have favorable thermodynamic properties for hydrogen desorption at moderate temperatures. However, experimental studies show that more than 300 °C is needed for hydrogen release from these compounds. In order to modify the hydrogen sorption properties of these compounds, partial substitution of $(BH_4)^-$ by halide ion (X^- = Cl^-, Br^-, I^-) have been investigated. The generation of the mixed phases $M(BH_4)_{2-x}X_x$ (M = Mg, Ca) was investigated by using in-situ and/or ex-situ synchrotron X-ray diffraction. The mixtures of $Mg(BH_4)_2$ and $MgCl_2$/$MgBr_2$ milled for 12 h shows shifts in the peak positions of β-$Mg(BH_4)_2$ after annealing at 200 °C as compared to pure β-$Mg(BH_4)_2$. The shifts correspond to a volume contraction of the unit cell of about 2% which is explained by substitution of Cl^- and Br^-, which has smaller ionic radius than $(BH_4)^-$, into the β-phase. In-situ PXD for the mixture of $Ca(BH_4)_2$ and $CaCl_2$ milled for 2 h shows phase transformation of α-$Ca(BH_4)_2$ to β-$Ca(BH_4)_2$ at 150-200 °C and the peaks for β-$Ca(BH_4)_2$ shift to higher angles with further heating. This is in agreement with substitution of $(BH_4)^-$ with smaller Cl^-. Hydrogen desorption temperature for the sample of $Mg(BH_4)_2$-$MgCl_2$/$MgBr_2$ was slightly decreased while the decomposition temperature of $Ca(BH_4)_2$ was slightly increased for the mixture of $CaBH_4$-$CaCl_2$. The samples of $Mg(BH_4)_2$-MgI_2 and $Ca(BH_4)_2$-$CaBr_2$ show no sign of substitution or formation of new phases.

Other Talks

Hauback, B.C.: Inorganic and materials chemistry in Norway: current status and future directions at IFE. Second National Meeting on Inorganic and Materials Chemistry, Sundvolden Hotell, Norway, October 11-12, 2012. Invited talk.

Sørby, M.H., Frommen, C., Olsen, J.E., Hauback, B.C.: Powder diffraction investigations of borohydrides. Second National Meeting on Inorganic and Materials Chemistry. Sundvolden Hotell, Norway, October 11-12, 2012.

Deledda, S., Guzik, M., Hauback. B.C.: Mg-based mixed transition-metal complex hydrides obtained by reactive milling. Second National Meeting on Inorganic and Materials Chemistry, Sundvolden Hotell, Norway, October 11-12, 2012.

Sartori,S. Talk: «When nano-confinement change the properties of hydrogen storage materials: the case of $Li^{11}BD_4$-$Mg(^{11}BD_4)_2$ and MgD_2 systems», Second National Meeting on Inorganic and Materials Chemistry. Sundvolden Hotell, Norway, October 11-12, 2012.

Hauback, B.C.: Energy storage – hydrogen stored in solid compounds a solution? KIFEE meeting, Trondheim, September 9-12, 2012. Invited talk.

Llamas-Jansa, I., Hauback, B.C.: Updates in-kind initiatives in Norway related to ESS. IKON2 meeting ESS, Malmø, Sweden, February 9-10, 2012. Invited talk.

Albanese, E., Kalantzopoulos, G., Vitillo, Pinatel, E., Civalleri, B., Deledda, S., Bordiga, S., Hauback, B.C., Baricco, M.: Theoretical and experimental study on $Mg(BH_4)_2$ -$Zn(BH_4)_2$ mixed borohydrides. International Symposium on Metal-Hydrogen Systems, Kyoto, Japan, October 21-26, 2012. Talk.

Baricco, M., Vitillo, J., Pinatel, E., Bordiga, S., Gil, E., Ju, J., Fichtner, M., *Kalantzopoulos, G., Deledda, S., Hauback, B.C.*, Dolci, F., Moretto, P.: Effect of additives on hydrogen sorption reactions in $LiNH_2/MgH_2$ mixtures prepared by ball milling. ISMANAN 2012, Moscow, Russia, June 18-21, 2012. Invited talk.

Floriano, R., Leiva, D.R., Moreira, A.J., *Deledda, S., Hauback, B.C.*, Botta, W.J.: Cold rolling of MgH_2 powders containing different additives (Fe, Nb, Fe_2O_3, Nb_2O_5 and FeF_3). NanoMat2012, Sao Carlos, Brazil, September 30 - October 2, 2012. Talk.

Mongstad, T., Mæhlen, J.P., You, C.C., Platzer-Björkman, C*., Hauback, B.C*., Karazhanov, S.: Photochromic thin films of oxygen-containing yttrium hydride. RERC Technoport Conference, Trondheim, April 16-18, 2012.

Pitt, M.P, Vullum, P.E., Sørby, M.H., Walmsley, J.C., Holmestad, R., Hauback, B.C.: Nanostructural studies of transition metal additives in $NaAlH_4$. Materials for Hydrogen Storage – Future Perspectives? June 14-18, 2012. Norwegian Coastal Express

International Schools

Sørby, M.H.: Instrumentation and research methods at IFE: Neutron scattering instrumentation at IFE. Oral presentation, 1st European Technical School on Hydrogen and Fuel Cells 2012, Heraklion (Creet), October 1-7, 2012.

Sørby, M.H.: Ground breaking research at IFE: Structure and property investigations of hydrogen storage materials. Oral presentation, 1st European Technical School on Hydrogen and Fuel Cells 2012, Heraklion (Creet), October 1-7, 2012.

Sartori, S. *«Hydrogen storage for vehicular applications»* Invited lecture: International School of Solid State Physics, 56th Course, *Materials for Renewable Energy,* Erice (Italy), July 18th – 28th, 2012.

2 ABSTRACT POSTERS

Materials Research Society Fall Meeting, Nov 26 – Dec 1, Boston, USA

Structure and sp2 Bond Character of Carbon Cones and Discs

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We show how the structure, degree of sp2 hybridization and covalent bond length of hollow carbon cones [1] and discs respond to ex- situ heat treatment up to 2700°C. The structure was investigated by selected area diffraction and high resolution imaging in the transmission electron microscope (TEM). The sp2 character and covalent bond length was determined by analyzing carbon K ionization edge spectra acquired with an electron energy loss spectrometer attached to the TEM. Results from these measurements show that the graphitic structural order and bond character increased significantly with heat treatment temperature. The evolution of the bond character of the cones was found to be slightly more similar to non-graphitizing carbons [2] than that of the 'graphitizing- carbon- like' discs [3]. This might be attributed to strain induced by the curved cone walls.

[1] Krishnan et al., Nature 388 (1997) 451
[2] Zhang et al., Carbon 49 (2011) 5049
[3] Daniels et al., Philosphical Magazine 87 (2007) 4073

EMC2012, September 16-21, Manchester, UK

Investigation of the Core and Edge Structure of Carbon Cones and Discs

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Keywords: Carbon cones and discs, structure, TEM

A rather peculiar polymorph of carbon; carbon cones, were first reported by Ge and Sattler in 1994 [1]. The cones they described exhibited an apex angle of ~19o. However, in 1997 cones with five distinct apex angles were discovered as a product of the Kvaerner Carbon Black and Hydrogen Process (CB&H) [2]. Krishnan et al. reported that the material resulting from the CB&H process contained 10% carbon black like particles, 70% flat carbon discs and 20% carbon cones [3]. Most importantly, they showed that the multiwalled cones exhibit discrete apex angles of 112.9˚, 84.6˚, 60˚, 38.9˚ and 19.2˚, corresponding to the incorporation of 1- 5 60˚ disclinations in a hexagonal graphitic sheet [3]. Note that the discs can be considered as cones with an apex angle of 180°. Both cones and discs exhibit sets of facets with angles θ1 = 22 ± 1° and θ2 = 60.0° - θ1, which has been explained by a shift of ± 21.8° between graphene layers yielding the most stable configuration [4, 5].

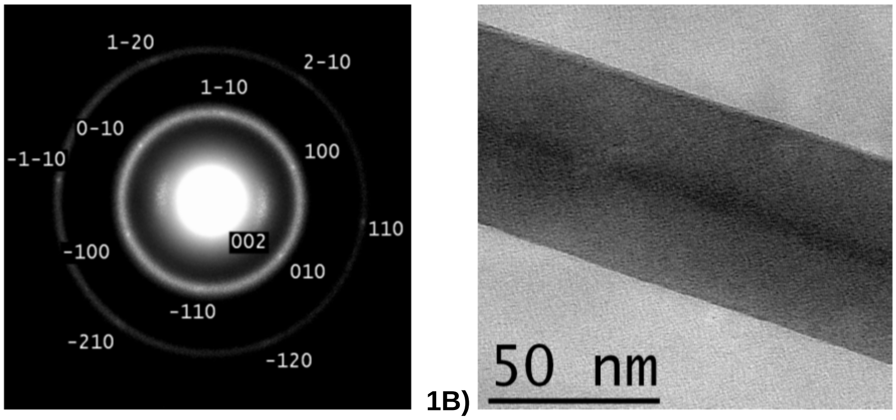
Due to the unique topography of the cones, they are promising for applications in hydrogen storage, sensors and electrodes [6]. Yu et al. have shown that hydrogen adsorbs on the surfaces of cones and discs produced by the CB&H process and suggest that electronic and adsorption properties at the edges might differ significantly from the rest of the surface of the particles [7]. Thus, it is of utmost importance to know the edge structure if any effect of edges on hydrogen storage is to be determined.

In the present study, '*as-produced*' and heat treated (HT) samples from the CB&H process have been studied in detail by combining different transmission electron microscopy (TEM) techniques; high resolution imaging (HREM), bright field (BF) and dark field imaging (DF), selected area electron diffraction (SAED), and energy filtered TEM imaging (EFTEM). HT of the sample was done at 2700°C for 3h in an argon atmosphere. The powder samples were suspended on holey carbon grids, while microtome sections were prepared (at Diatome AG) by embedding the carbon powder in an epoxy resin, cutting with a feed of 50nm and subsequently suspending sections on holey carbon grids. All samples were investigated with a Jeol JEM2010F microscope; equipped with an ultra high resolution pole piece and Gatan Image Filter (GIF200), operated at 197kV. HREM micrographs were obtained quickly in order to minimize irradiation damage to the samples.

The focus of the present study is on structure of the edges, graphitisation and domains. SAED patterns of as produced carbon carbon discs (Figure 1A) exhibit both diffuse rings and a set of distinct reflections. This suggests that carbon discs contain a graphitic core surrounded by more disordered carbon in agreement with [5]. Due to the relative intensities of the diffracted spots, it has been suggested that a graphitic core comprises of approximately 10-30% of all the material in a disc. BF images of microtome cross sections (Figure 1B) confirm the existence of a core within 'as produced' carbon discs. Here, the darker contrast of the central region indicates a denser (i.e. more graphitic) structure. The width of the core is ~8.5 nm thick and represents ~15% of the total volume of the disc, which is in agreement with calculated core size estimate of Næss et al. [5]. By SAED, EFTEM, HREM and DF micrographs, carbon cones and discs were determined to exhibit a closed curved edge structure, as can be seen for the open end of a HT cone in Figure 2. Here, the closed edge exists throughout the cone and the initial core cannot be distinguished from the rest of the cone. Although HT significantly increases the graphitic order, the curved edge topography was found for all cones and discs independent of treatment. Micrographs of HT cones and discs (not shown here) exhibit Moiré fringes consistent with crystalline domains within the particles. Here, domains are several hundred nanometres in diameter, which is inconsistent with the previously reported coherence length of 20nm [5]. [8].

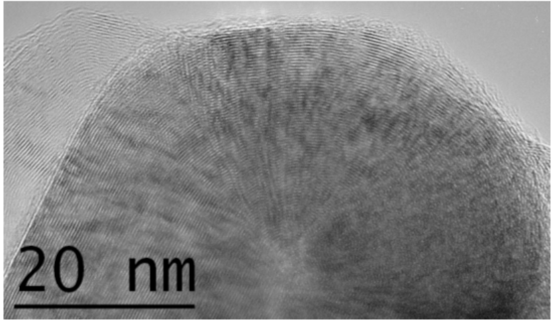
References
[1] M Ge and K Sattler, Chemical Physics Letters **220** (1994), p. 192.
[2] JA Bakken *et al*, Pure and Applied Chemistry **70** (1998) p.1223.
[3] A Krishnan *et al*, Nature **388** (1997) p. 451.
[4] T Garberg *et al*, Carbon **46** (2008) p. 1535.
[5] SN Naess *et al*, Science and Technology of Advanced Materials **10** (2009) p. 065002.
[6] J Muller *et al*, Y. Magarshak (ed.), *Silicon Versus Carbon*, Springer Netherlands**,** (2009), p. 285.
[7] X Yu *et al*, Applied Surface Science **255** (2008), p. 1906.
[8] This work was supported by the Research Council of Norway under contract no. 191621/V30.

The authors thank Helmut Gnägi of Diatome AG for preparing the microtome sections.



1A) **1B)**

Figure 1A: *SAD pattern of an 'as produced' carbon disc showing a set of discrete reflections corresponding to crystalline region within the C nanodisc.*
1B: *Bright field image of a microtome cross section of a 56 nm thick nanodisc showing direct evidence of the position a crystalline region (8.5 nm) in the core of the nanodisc.*



2)

Figure 2*: A HREM micrograph of the open ended edge of a HT carbon cone exhibiting a curved and closedstructure throughout the cone.*

EMC2012, September 17-21, Manchester, UK

STEM- EELS Low Loss Mapping of Carbon Nanocones

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Keywords: carbon, cones, EELS.

Carbon nanocones distinguish themselves from the myriad of known carbon nanostructures by exhibiting discrete apex angles (112.9˚, 84.6˚, 60˚, 38.9˚ and 19.2˚) corresponding to the incorporation of 1 to 5 60˚ disclinations in a hexagonal graphitic sheet [1]. This topography makes the hollow, multiwalled cones very promising for applications in hydrogen storage, sensors and electrodes [2]. The cone samples investigated in this study were produced from crude oil with a plasma arc, and contain a large number of flat discs, which themselves can be considered cones with an apex angle of 180°.

It is of great interest to determine the electronic structure of individual cones for potential future applications. For example; any variation of the electronic structure as function of cone geometry (i.e.apex angle) would have to be taken into careful consideration before any practical application in sensor technology. Electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM- EELS) provides the perfect tool for these investigations due to its high combined spatial and energy resolution. All data shown here were acquired with a Nion UltraSTEM operated at 60kV to minimize irradiation damage to the carbon cones, with a measured energy spread of 0.30eV. EEL spectra were deconvoluted for thickness and then de-noised using multivariate statistical analysis as implemented in the HREM Research MSA plug-in for Digital Micrograph [3].

The spatial distribution of the dielectric response of carbon nanotubes and carbon onions has previously been investigated by M. Kociak et al. [4]. This was done by comparing results of low loss EELS line scans to the corresponding High Angle Annular Dark Field (HAADF) image intensity profiles. They identified the observed plasmon modes by comparing the acquired EEL spectra to semi-classical simulations of surface plasmon excitations in EEL spectra of carbon onions, relating specific modes to either the in-plane or out-of-plane component of the dielectric tensor [4].

In the present study we have extended the approach of M. Kociak et al. [4] to mapping of the relative contribution and spatial distribution of plasmon modes. This was done by acquiring 2-D EELS low loss spectrum images of suspended carbon nanocones, for all five discrete cone geometries. *Ab initio* simulations using density functional theory are currently being carried out to model the valence structure of the cones and explain the observed plasmonic distributions. In this study, the tip area of cones was investigated with particular scrutiny. An example of this is shown in Figure 1 for a cone with 4 pentagons at the tip (i.e. corresponding to an apex angle of ~38.9°: Figure 1a). The EELS low loss map in Figure 1b shows an intriguing spatial distribution of the excitation of a surface plasmon mode attributed to both π→σ* and σ→π* transitions [4]. The map was integrated over a 4eV window as indicated for the spectrum in Figure 1c. By comparing the EELS map (Figure1b) to the HAADF micrograph in (Figure 1a), it is clear the relative intensity of the 'π→σ*/ σ→π*' mode peaks at the edge (i.e. the surface) of the cone.

References

[1] A. Krishnan *et al*, Nature, **388** (1997) p.451
[2] J. Muller *et al*, in 'Silicon Versus Carbon', ed. Y. Magarshak, S. Kozyrev and A.K. Vaseashta, 2009 p. 285
[3] M. Watanabe *et al*, Microsc. Microanal, **13** (2007) p.1264
[4] M. Kociak *et al*, Phys. Rev. B, **61** (2000) p.13936
[5] The authors gratefully acknowledge funding from the Research Council of Norway under grant number 191621/V30. SuperSTEM is funded by EPSRC as the National Facility for Aberration Corrected STEM, located at Daresbury Laboratories.

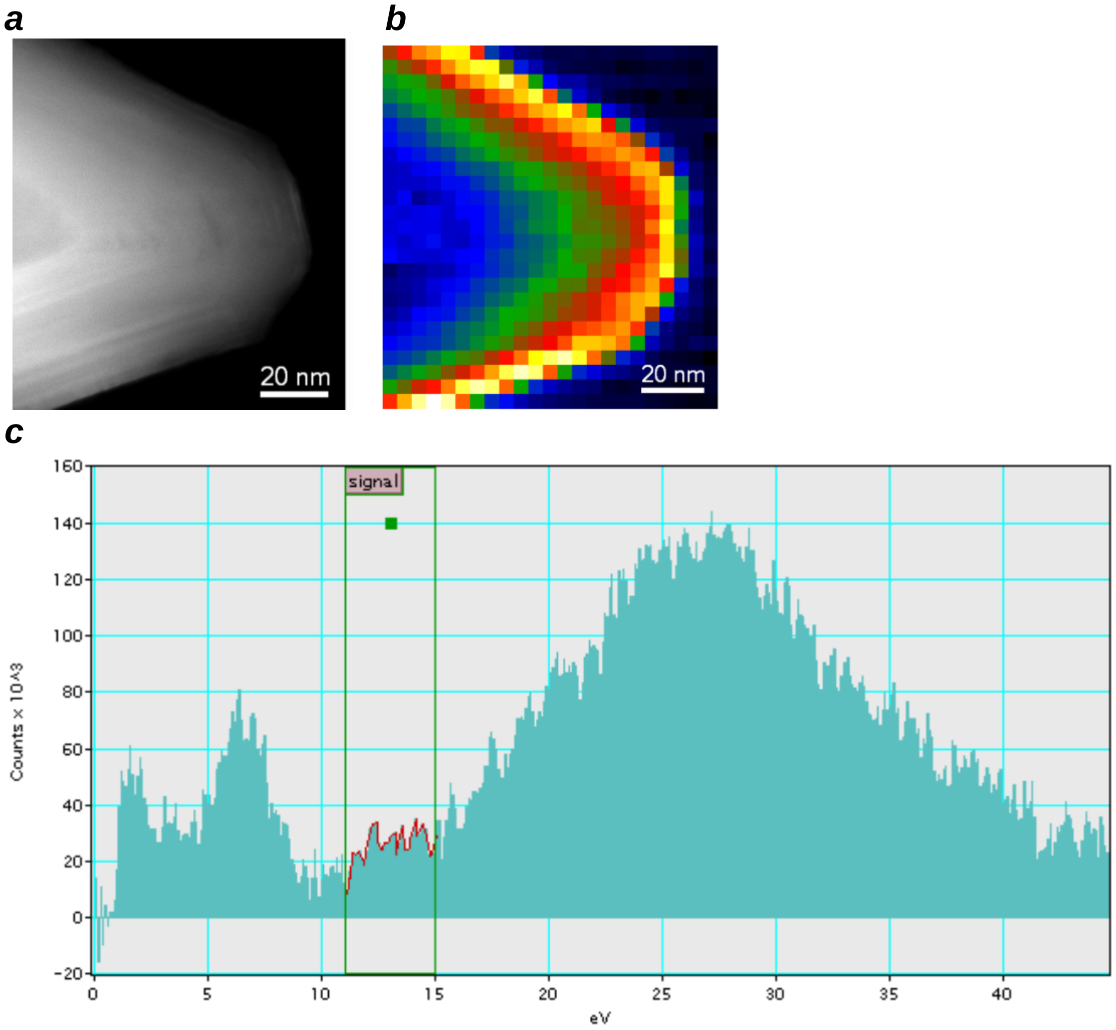

Figure 1a. *HAADF micrograph of the tip of a carbon nanocone (4 pentagons at the tip)* **b.** *EELS low loss map showing the spatial distribution of the excitation of the 'π→σ*/ σ→π*' surface plasmon mode. This map was integrated over a 4eV window as indicated in the low loss spectrum* **c** *(zero loss peak stripped)***.**

Materials Research Society Fall Meeting, Nov 26 –Dec 1, Boston, USA

Magnetic Properties of Carbon Nanodisks and Nanocones Powder

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We have investigated the magnetic properties of carbon powders which consist of nanodisks, nanocones and a small fraction of carbon black particles. Magnetization measurements were carried out using a supercomputing quantum interface device (SQUID) in magnetic fields $-5 < B < 5$ T for temperature $2 < T < 350$ K. In the temperature range $2 < T < 10$ K and after subtraction of the diamagnetic background, the magnetization shows a strong paramagnetic temperature dependence and this cannot be fitted to a Curie law. At $T = 2$ K, magnetization versus magnetic field shows a paramagnetic free spin behavior in the case when $B/T > 1$T/K, which could be a signature of electron localization in high magnetic fields at low temperature. This is in agreement with an electron g-factor close to the free electron value $g=2.002$ measured by EPR in these samples. Magnetization measurements also show an additional weak ferromagnetic contribution which is clearly higher than what can be attributed to a low level (< 100 ppm) of Fe impurities found in the samples.

SYNKNØYT (user meeting), January 30-31, Stavanger, Norway

Halide Substitution in Borohydrides Studied by Synchrotron X-ray Diffraction

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Alkali and alkaline earth metal borohydrides have been investigated as one of the most promising hydrogen storage materials for mobile use because of their high gravimetric hydrogen capacity. Among them, $Mg(BH_4)_2$ and $Ca(BH_4)_2$ contain large amount of hydrogen of 14.9 and 11.6 mass %, respectively, and it is predicted that these compounds have favorable thermodynamic properties for hydrogen desorption at moderate temperatures. However, experimental studies show > 300 °C is needed for hydrogen release from these compounds. In order to modify hydrogen storage properties of these compounds, partial substitution of $(BH_4)^-$ by halide ion ($X^- = Cl^-, Br^-, I^-$) have been investigated in this study. The generation of the mixed phase $M(BH_4)_{2-x}X_x$ (M = Mg, Ca) was investigated by using in-situ and/or ex-situ synchrotron X-ray diffraction. The mixtures of $Mg(BH_4)_2$ and $MgCl_2$/$MgBr_2$ milled for 12 h shows shifts in the peak positions of β-$Mg(BH_4)_2$ after annealing at 200 °C as compared to pure β-$Mg(BH_4)_2$. The shifts correspond to a volume contraction of the unit cell of about 2% which is explained by substitution of Cl^- and Br^-, which has smaller ionic radius than $(BH_4)^-$, into the β-phase. In-situ PXD for the mixture of $Ca(BH_4)_2$ and $CaCl_2$ milled for 2 h shows phase transformation of α-$Ca(BH_4)_2$ to β-$Ca(BH_4)_2$ at 150-200 °C and the peaks for β-$Ca(BH_4)_2$ shift to higher angles with further heating. This is in agreement with substitution of $(BH_4)^-$ with smaller Cl^-. Hydrogen desorption temperature for the sample of $Mg(BH_4)_2$-$MgCl_2$/$MgBr_2$ was slightly decreased while the decomposition temperature of $Ca(BH_4)_2$ was slightly increased for the mixture of $CaBH_4$-$CaCl_2$. The samples of $Mg(BH_4)_2$-MgI_2 and $Ca(BH_4)_2$-$CaBr_2$ show no sign of substitution or formation of new phases.

MH2012, October 21-26, Kyoto, Japan

In-situ Regeneration of NaAlH4 and LiAlH4 by NMR Spectroscopy

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The hydrogenation pathway of complex hydrides has been highly debated in recent years. The foremost reason for this is the dearth of analytical techniques available to characterize the intermediates synthesized during the hydrogenation process. NMR spectroscopy has the ability to detect all phases contained within a matrix, whether or not they are crystalline, thus it has proven to be an excellent complement in the study of complex hydrides, especially borohydrides. In-situ NMR spectroscopy has been utilized in determining the dehydrogenation pathway of many hydrides [1, 2], but the inability to pressurize samples under H2 during experiments has inhibited this technique for hydrogenation reactions.

The in-situ hydrogenation of decomposed NaAlH4 (1) and LiAlH4 (2) has been studied using a high pressure NMR cell. The hydrogenation of decomposed NaAlH4 was studied by 27Al and 23Na wide line NMR spectroscopy, while 7Li and 27Al was studied for LiAlH4. The hydrogenation of decomposed NaAlH4 was the most intriguing, a peak corresponding to Na3AlH4 is observed within two minutes of hydrogenation, followed by the insurgence of NaAlH4 after only four minutes. The in-situ hydrogenation of LiAlH4 has not been previously measured due to the fact that the reaction takes place as a slurry. NMR spectroscopy is perfect for these measurements and corroberates the synthesis reported previously by Ashby [3] and Graetz [4]. As predicted, LiAlH4 is formed without a preceding hexahydride intermediate to form the solvated tetrahydride.

$$\mathrm{NaH + Al \xrightarrow[\text{2 mol\% TiCl}_3]{\text{140 bar H}_2\text{, 120 °C}} NaAlH_4} \tag{1}$$

$$\mathrm{LiH + Al \xrightarrow[\text{THF, 0.5 mol\% TiCl}_3]{\text{35 bar H}_2\text{, 40 °C}} LiAlH_4{\cdot}4THF} \tag{2}$$

References

[1] M.H.W. Verkuijlen, P.J.M. van Bentum, O. Zabara, M. Fichtner, A.P.M. Kentgens, J. Phys. Chem. C, 115 (2011) 13100.
[2] J.W. Wiench, V.P. Balema, V.K. Pecharsky, M. Pruski, J. Solid State Chem., 177 (2004) 648.
[3] E.C. Ashby, H.E. Redman, G.J. Brendel, Inorg. Chem., 2 (1963) 499.
[4] J. Graetz, J. Wegrzyn, J.J. Reilly, J. Am. Chem. Soc., 130 (2008) 17790.

Destabilization Effect of Transition Metal Fluorides on Sodium Borohydride

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In this study, we explore the products of ball-milling between $NaBH_4$ and TiF_3, MnF_3 or FeF_3, as well as the effect of the transition metal fluorides on the decomposition of $NaBH_4$. Pressure and temperature evolution were monitored during ball-milling of the materials. The as-milled powders are examined by Thermal Programmed Desorption (TPD) with Residual Gas Analysis (RGA), and Thermo Gravimetric Analysis (TGA). The structure of the as-milled materials was investigated by *in situ* PXD up to 600 °C. Pure $NaBH_4$ displays an onset temperature of hydrogen release of 430 °C [1]. Ball-milling $NaBH_4$ with MnF_3 results in a composite system with onset temperature for hydrogen release of 130 °C, whereas FeF_3 and TiF_3 decrease the onset temperature for hydrogen release to 161 °C and to 265 °C, respectively, as Figure 1 shows. Emissions of volatile B-H species during hydrogen release are negligible.

Data from powder diffraction analysis analyzed by Rietveld refinement will be discussed with respect to phase selection processes that occur during ball-milling and during *in situ* heating of the as-milled powders. The effect of the different TMF_3 on the selective release of H_2 instead of B_2H_6 which is observed by residual gas analysis will be also discussed. Finally, the reversibility of the examined systems will be critically assessed.

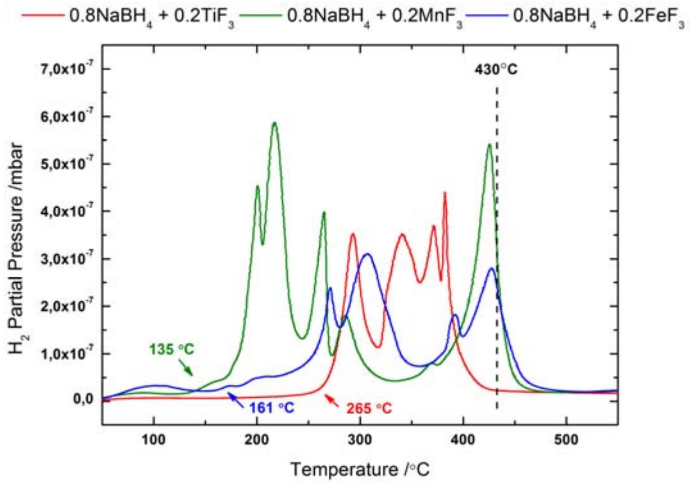

Figure 1. TPD with RGA of the as-milled phases. Heating rate is 2°C/min.

References

[1] J. Urgnani, F.J. Torres, M. Palumbo, M. Baricco, Hydrogen release from solid state NaBH4, Int. J. Hydrog. Energy, 33 (2008) 3111-3115.

6^{th} Int. Symposium Hydrogen & Energy (Empa) January 22-27, Stoos, Switzerland

Mechanochemical Reaction of Sodium Borohydride with Transition Metal Fluorides

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In this study we are exploring the effect of the mechano-chemical reaction between $NaBH_4$ and transition metal fluorides. Pressure and temperature evolution have been monitored during the mixing of the materials. The compounds have been examined by TPD and DSC studying the gas release temperature and melting temperature respectively. The structure of the ball milled compounds in elevated temperatures was investigated by *In-situ* PXD.

Ball milling techniques are widely used as a synthesis technique of potential hydrogen storage materials. The grain-size reduction process that takes place during continuous and vigorous fracturing occurs from mixing of powder particles enhancing the possibility of interaction between them [1]. The produced compounds can exhibit altered thermodynamic properties. The energy offered due to the mechanochemical reaction can favour the formation of new phases [2]. Borohydrides are materials that recently have attracted lot of attention as potential hydrogen storage materials. The mixture of borohydrides with other compounds can lead to the formation of phases with attractive thermodynamic properties [3].

Powder mixtures of $NaBH_4$ and transition metal fluorides with 4:1 ratio were ball-milled in Ar using a Fritsch P6 planetary ball mill. The ball-to-powder ratio was 100:1. Differential Scanning Calorimetry (DSC) measurements were performed with a SensysDSC from Setaram. Samples were placed in high-pressure capable stainless steel crucible (p_{max} = 500 bar; T_{max} = 600 ^{o}C) and data were collected upon heating and cooling in Ar flow (15 ml/min) using a constant rate of 2 ^{o}C/min. Gas release was examined using a home-made apparatus for Thermal Programmed Desorption (TPD) coupled with a MULTIVISION IP detector system for residual gas detection analysis. Measurements were carried out in vacuum (10^{-5} mbar) between RT and 600 ^{o}C. High temperature powder x-ray patterns were collected using an imaging plate system (MAR345) with an exposure time of 30 s.

Results for 4 $NaBH_4$ + TMF_3 (TM = Fe, Mn, Ti) will be presented. Data from diffraction analysis will be discussed with respect to phase selection processes that occur during ball-milling and during in-situ heating of the as-milled powders. DSC and TPD show changes in the thermal stability of the milling products, depending on the TMF_3 used as a starting material. The effect of the different TMF_3 on the selective release of H_2 instead of B_2H_6 which is investigated by residual gas analysis will be also discussed.

References

[1]Zaluska, *et al.*, J. Alloys Compounds, 288, (1999), 217.

[2]Zhang, *et al.*, J. Alloys Compounds, 393, (2005), 147.

[3] Hai-Wen Li, *et al.*, Energies, 4, (2011), 185-214.

Materials Research Society Fall Meeting, Nov 26 –Dec 1, Boston, USA,

Dielectrophoresis in Preparing Functional Polymer Composites with Assembled Nanoparticles

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[2] *Department of Physics, Norwegian University of Science and Technology, Trondheim, Norway;*
[3] *Mads Clausen Institute, University of Southern Denmark, Sønderborg, Denmark;* [4] *Department of Physics, University of Oslo, Oslo, Norway.*

We use an alternating electric field (dielectrophoretic effect) to align electrically conductive particles such as carbon black, graphene nanoparticles etc. into single wirelike strings in a polymer matrix. Particle alignment makes the material conductive and curing the matrix stabilizes the strings. These materials can act as micro-mechanical strain sensors and for instance stretching the aligned strings leads to a reversible change in resistivity with a gauge factor of 150. In general, this method allows us to use low particle fraction (<<1 vol. %) which leads to various benefits such as enhanced transparency as compared to the conventional conductive composites.

SAS2012, November 18-23, Sydney, Australia

Heating induced swelling of Na-fluorohectorite clay

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Clays are of paramount importance for soil stability[1], but also in applications ranging from oil recovery[2] to composites[3] and hydrogels[4]. Generically, clays are divided into two subclasses: macroscopically swelling, 'active' clays that have the capacity for taking up large amounts of water to form stable gels, and 'passive' or non-swelling clays; the former stabilize soils whereas the latter are known to lead to landslides[5].

However, it has been unclear so far what mechanisms underlie clay swelling. Here, we report the first observation of a temperature-induced transition from a passive to an active, swelling clay. We propose a simple description of the swelling transition; while net attractive interactions are dominant at low temperatures so that the clay particles remain attached to each other in stacks, at higher temperatures it is energetically favourable for the clay

SYNKNØYT (user meeting), January 30-31, Stavanger, Norway

Polymer Nanostructures Elucidated via Small-Angle Neutron Scattering

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A range of interesting water-soluble polymers with different functionality has recently been designed in the group of B. Nyström at the Univ. of Oslo. One example is a linear-chain ABCBA penta-block polymer that contains a hydrophobic PNIPAAM block to each side of a hydrophilic PEG segment, and negatively charged PSSS groups at the ends. For this system there will be a competition between the attractive force of the hydrophobic blocks, the repulsion between the charged groups, and the tendency for the hydrophilic group to maximize the interaction with the surrounding water.

The polymer has been made in two versions, with different lengths of the hydrophilic block (PEG), having 34 and 77 C-atoms, respectively. We observe that the physical properties of the system are highly dependent on the length of this block. A sharp and highly reproducible temperature-induced transition, related to nanoparticle formation, is observed at a temperature just below 40 C, as well as drastic and reproducible changes in viscosity. Small-angle neutron scattering can be used to gain important structural information on this type of polymer systems.

NSSM2012, January 18-19, Gøteborg, Sweden

Temperature-induced Changes in a new ABCBA Polymer

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A new linear-chain water-soluble ABCBA pentablock polymer has been designed. This polymer has a hydrophobic PNIPAAM block (B) to each side of a hydrophilic PEG segment (C), and negatively charged PSSS groups (A) at the ends. For this system there will be a competition between the attractive force of the hydrophobic blocks, the repulsion between the charged groups, and the tendency for the hydrophilic group to maximize the interaction with the surrounding water.

The polymer has been made in two versions, with different lengths of the hydrophilic block (C), having 34 and 77 C-atoms, respectively. We observe that the physical properties of the system are highly dependent on the length of this C block. A sharp and highly reproducible temperature-induced transition, related to changes in chain conformation, is observed at a temperature around 40 C, as well as drastic and reproducible changes in viscosity.

SYNKNØYT (user meeting), January 30-31, Stavanger, Norway

Decomposition Study of $Yb(BH_4)_3$

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Hydrogen can act as an energy carrier and substitute fossil fuels in both stationary and mobile applications. Ongoing research shows that metal borohydrides can store hydrogen in a safe and efficient way, with high gravimetric hydrogen densities and volumetric densities significantly exceeding those in compressed gas or liquid hydrogen. However, most of the light metal borohydrides are thermodynamically too stable for storage applications.

Recently transition metal and rare-earth metal borohydrides have been synthesized by mixing the respective metal chloride with a simple alkali metal borohydride[1-3]. Here we present the results for ytterbium.

Mechanochemical processing of $YbCl_3$ with $LiBH_4$ results in several phases. Short reaction time results in an unknown phase with primitive cubic unit cell, a = 6.16 Å. This phase is probably a Li-Yb-BH_4-Cl phase since it transforms into $Yb(BH_4)_3$ and LiCl after longer reaction times. There are two $Yb(BH_4)_3$-modifications, α-$Yb(BH_4)_3$ Pa-3 ($a \approx 10.75$) and a metastable β-$Yb(BH_4)_3$ Fm3c ($a \approx 10.9$) as determined from powder synchrotron diffraction (SR-PXD) at SNBL. The decomposition path of this mixture has been studied using in situ SR-PXD at SNBL. The decomposition goes through several steps. The structure of the different decomposition products and the initial phase are also under investigation by powder neutron diffraction at IFE and will be presented at the meeting.

1. Frommen, C., et al., *Crystal structure, polymorphism, and thermal properties of yttrium borohydride Y(BH(4))(3).* Journal of Alloys and Compounds, 2010. **496**(1-2): p. 710-716.
2. Frommen, C., et al., *Synthesis, Crystal Structure, and Thermal Properties of the First Mixed-Metal and Anion-Substituted Rare Earth Borohydride LiCe(BH4)3Cl.* The Journal of Physical Chemistry C, 2011. **115**(47): p. 23591-23602.
3. Rude, L.H., et al., *Tailoring properties of borohydrides for hydrogen storage: A review.* Physica Status Solidi a-Applications and Materials Science, 2011. **208**(8): p. 1754-1773.

MarchCOMeeting'12, March 6-9, Havanna, Cuba

Phase Separations in PNIPA-Laponite Nanocomposites

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Poly-N-isopropylacrylamide-Laponite nanocomposites hydrogels (NC-gels) have recently been synthesized by Haraguchi et al [1], and the mechanisms during formation of the three-dimensionally cross linked polymer have been presented in several papers [2-4]. These gels exhibit superior mechanical properties compared to organically cross linked hydrogels, and they are also transparent, in contrast to their organic counterparts.

Formation of a visible ring in the transparent PNIPA-Laponite NC-gel during polymerization was observed by our group, and it was recognized that this was due to oxygen contamination during sample preparation. The ring was found out to be the end of the three-dimensionally cross linked polymer, and acted as a kind of barrier between the polymer rich phase at the bottom and the water-rich phase at the top. The top layer mainly consists of unreacted monomer and clay-brush particles suspended in the water. The depth of the top layer is influenced by both the oxygen content in the sample vial, and the concentration of Laponite in the initial solution before polymerization. Samples with different clay content were monitored with a movie recorder during polymerization. The movies showed a clear correlation between the amount of clay and the thickness of the polymer rich phase, and also the time for the polymerization reactions to finish. More clay led to thicker polymer phases and longer polymerization times. None of the phenomena mentioned above occurred if the samples were kept under oxygen-free environment during preparation and polymerization.

[1] Haraguchi, K.; Takehisa, T., Nanocomposite hydrogels: A unique organic-inorganic network structure with extraordinary mechanical, optical, and swelling/de-swelling properties. *Advanced Materials* **2002,** 14, (16), 1120-1124.

[2] Shibayama, M.; Karino, T.; Miyazaki, S.; Okabe, S.; Takehisa, T.; Haraguchi, K., Small-angle neutron scattering study on uniaxially stretched poly(N-isopropylacrylamide)-clay nanocomposite gels. *Macromolecules* **2005,** 38, (26), 10772-10781.

[3] Abdurrahmanoglu, S.; Okay, O., Rheological Behavior of Polymer-Clay Nanocomposite Hydrogels: Effect of Nanoscale Interactions. *Journal of Applied Polymer Science* **2010,** 116, (4), 2328-2335.

[4] Haraguchi, K.; Li, H. J.; Matsuda, K.; Takehisa, T.; Elliott, E., Mechanism of forming organic/inorganic network structures during in-situ free-radical polymerization in PNIPA-clay nanocomposite hydrogels. *Macromolecules* **2005,** 38, (8), 3482-3490.

[5] Haraguchi, K. and T. Takehisa, *Advanced Materials*, 2002. **14**(16): p. 1120-1124.

Synthesis and Characterisation of Polystyrene-Clay Nanocomposites

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Recent progress in polymer science has demonstrated that remarkable changes in material properties are achievable by combining polymer systems with miniature particles, where at least one of the particle dimensions is in the nanosize range. Even minute quantities (sometimes less than 1 5) can drastically modify the overall system behavior if the surface of the incorporated particles has been made to interact sufficiently with the polymer chains. Fu et al [1] dispersed organically modified montmorillonite clay into polystyrene (PS), and increased the dynamic modulus of the nanocomposite by over 60 %, with only 8 wt-% filler material. We recently started to build upon Fu et al's work on PS-clay systems, by incorporating other types of smectic clays, such as Laponite and Fluorohectorite, and also manipulating the orientation and super structure of the clay particles with electric fields. The presentation will give a brief summary of the synthesis and characterization of such composites.

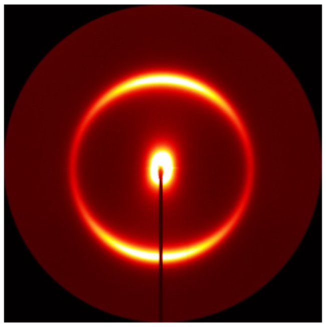

Figure 2: SAXS scattering pattern of PS-fluorohectorite composite.

[1] X. Fu and S. Qutubuddin, Materials Letters 42 (2000) 12.

SYNKNØYT (user meeting), January 30-31, Stavanger, Norway

Investigation of $Ca(BH_4)_2$ by Neutron and Synchrotron Radiation

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Future increase in demand for energy requires development of alternative methods to store and convert energy. Regarding road transportation fuel, the use of hydrogen as an energy carrier is considered a very attractive solution. A major challenge for the introduction of hydrogen as an energy carrier for mobile applications is safe and efficient storage of hydrogen. The conventional ways are to store hydrogen either as pressurized gas in high pressure tanks or as cryogenic liquid. However, both these methods suffer from major drawbacks concerning i.e. energy consumption and safety.

A method which can store hydrogen very efficiently is storage in solid compounds, e.g. metal hydrides. The complex hydride $Ca(BH_4)_2$ is a compound potentially very suitable for hydrogen storage purposes due to high volumetric and gravimetric capacity for hydrogen as well as suitable thermodynamic properties according to the predicted decomposition reaction. However, experimental work done so far shows a more complex decomposition pathway including formation of unknown intermediate phases, as well as high decomposition temperature and severe reversibility. In order to be able to improve sorption properties and to clarify suitability as hydrogen storage material, detailed knowledge about decomposition mechanisms and reaction pathway is of crucial importance.

We have studied the decomposition products formed from thermal decomposition of $Ca(BH_4)_2$ by *in-situ* synchrotron x-ray diffraction (SR-PXD), high resolution SR-PXD measurements and neutron diffraction. The data provides detailed information on the phase transformations during decomposition, and two of the unknown intermediate phases have been identified and structure models proposed. In addition to diffraction studies for investigation of the decomposition route, quasi-elastic neutron scattering (QENS) was performed to obtain information about hydrogen dynamics. Rotational and translational diffusion of H and the H-rich species were investigated by QENS measurements performed at two complementary instruments with different energy resolution, and theoretical calculations (DFT) were used to identify the possible dynamic events. The presented work was the first QENS study on $Ca(BH_4)_2$, and the combined DFT-QENS approach was shown to be a strong tool in the interpretation of the data.

Complex Workshop, January 30 – February 5, Porto de Galinhas, Brasil

CO_2 and Porous Media - SANS

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We are presently involved in research activities focusing on physical processes that are important for the understanding of CO_2 transport and storage into the ground. The relevant geological structures may show large variations in composition (water saturated porous materials, such as sandstone in a sedimentary basin, caprock, clays). CO_2 trapped in such porous materials relies on different mechanisms of confinement that act on different time scales. Some important factors to consider are: 1) an impermeable caprock that keeps the fluid underground (supercritical CO_2 fluid), 2) the solubility of the CO_2 in the water, 3) intercalation (absorption) into clay nanopores, 4) chemical reactions that bind the carbon in mineral form to the rock.

Small Angle Neutron Scattering (SANS) is a technique highly valuable for studying nanostructures (1-100nm), such as clays nanoparticl*es*, and this technique is available at Institute for Energy Technology (IFE). For the investigations on CO2 and porous materials we will make use of a specially designed cell to be used in combination with SANS. The cell allows studying nanoporous materials together with CO_2 in the supercritical state, up to 150°C and CO_2 pressure up to 690 bars. A specially adapted setup has now been made in order to integrate this CO_2 cell into the SANS apparatus. In addition, the instrument has been upgraded by the implementation of a new element - a so-called bender. This is designed to deflect neutrons with wavelengths above 4.5 Å by a certain amount (4°), thus removing fast neutrons and gamma radiation, in order to improve the quality of the neutron beam.

Complex Workshop, May 22-25, Svolvær, Norway

Dynamic Light Scattering measurements of clay materials in liquid CO2

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Dynamic Light Scattering (DLS) is more and more widely used technique to study nanomaterials (10-1000nm) in different solvents. The DLS technique is very simple, fast and convenient technique. It allows obtaining absolute measurements of several parameters of interest, like molecular weight, radius of gyration, translational diffusion constant and so on, it also has modest development costs.

To study different nanomaterials we used the CO2 cell primarily designated for SANS measurements. The design of the CO2 cell allowed us to apply the DLS in backscattering mode. In backscattering mode the angle between the incident light beam and the scattered light was in the range 140-175 degrees. The CO2 cell allows studying materials in different pressure and temperature conditions, including liquid and supercritical state of CO2, up to 150°C and pressure of CO2 up to 414 and, what is very important for us, using different non-aggressive solvents (water and heavy water, alcohols or liquid CO2).

The cell is designed to study materials like caprock or clays for geologic storage of CO2. CO2 storage in deep geological structures is a complex physico-chemical process and the geometry of pore space (pore size distribution and total porosity) is important characteristic of these materials. The DLS technique could help to understand the thermodynamic behavior of clay particles interacting with liquid CO2 and can be used as complementary technique with SANS.

Our present research focuses on physical processes that are of importance for the optimization and understanding of CO2 transport into the ground. The relevant geological structures may show large variations in composition (water saturated porous materials, such as sandstone in a sedimentary basin, caprock, clays). CO2 trapped in such porous materials relies on different mechanisms of confinement that act on different time scales. Some important factors to consider are: 1) an impermeable caprock that keeps the fluid underground (supercritical CO2 fluid), 2) the solubility of the CO2 in the water, 3) intercalation (absorption) into clay nanopores, 4) chemical reactions that bind the carbon in mineral form to the rock.

To validate the applying of the CO2 cell for the DLS measurements, polystyrene spheres (100nm and 200nm in diameter) were used. The results showed very good agreement of diameter values with the real ones.

Preliminary DLS measurements of laponite clay in H2O showed satisfying agreement of particle dimensions and hydrodynamic properties with the real values. The measurements in liquid CO2 were harder to perform because the CO2 viscosity is 2 orders of magnitude lower then water causing faster sedimentation of clay particles. Nevertheless, results obtained from clay particles in CO2 are very promising.

Other Posters

Llamas-Jansa, I., Cai, X., X., Deledda, S., Sørby, M.H., Knudsen, K., Helgesen, G., Hall-Wilton, R., Hauback, B.C.: Norwegian Work Package: JEEP II neutron reactor. Science and Scientists at ESS, Berlin, Germany, April 18-20, 2012. Poster.

Cai, X.X., Llamas-Jansa, I., Hval, S., Mullet, S., Hall-Wilton, R., Hauback, B.C.: Modelling the JEEP II reactor using Geant4. IKON-3, Lund, Sweden. September 19-21, 2012. Poster.

Humphries, T.D., Birkmere, D., Hauback, B.C., Jensen, C.M.: In-situ Regeneration of $NaAlH_4$ and $LiAlH_4$ by NMR Spectroscopy. Second National Meeting on Inorganic and Materials Chemistry, Sundvolden Hotell, October 11-12, 2012. Poster.

Sobas, P., Knudsen, K.D., Helgesen, G., Skjeltorp, A. T., Måløy, K.J., Fossum, J.O.: "Dynamic Light Scattering measurements of clay materials in liquid CO_2: Preliminary results". CLIMIT seminar, Oslo, Nov 29-30, 2012. Poster.

Blanchard, D., Maronsson. J.B., Riktor, M.D., Kehres, J. Sveinbjörnsson, D., Gil Bardaji, E., Leon, A., Juranyi, F., Wuttke, J., Lefmann, K., Hauback, B.C., Ficthner, M., Vegge, T.: Hydrogen dynamics in Ca- and Mg-borohydrides studied with QENS and DFT calculations. International Symposium on Metal-Hydrogen Systems, Kyoto, Japan, October 21-26, 2012. Poster.

Taube, K., Pistidda, C., Dornheim, M., Velez-Bracho, V.M., Vila, M.T.E., Martinez, C.L., Zoz, H., Ren, H., Kríž, O., Keder, R., Jensen, T.R., Deledda, S., Hauback, B.C., Baricco, M., Züttel, A., Charalambopoulou, G., Stubos, A., Steriotis, T.: BOR4STORE: Fast, reliable and cost effective boron hydride based high capacity solid state hydrogen storage materials. International Symposium on Metal-Hydrogen Systems, Kyoto, Japan, October 21-26, 2012. Poster.

Rude, L.H., Hino, S., Hauback, B.C., Skibsted, J., Jensen, T.R.: Preparation and characterization of fluoride substituted metal borohydrides. International Symposium on Metal-Hydrogen Systems, Kyoto, Japan, October 21-26, 2012. Poster.

Hansen, E.L., Hemmen, H., Fonseca, D.M., Coutant, C., Anmarkrud, Ø.L., Fossum, J.O., Knudsen, K.D., Plivelic, T.: "The effects of temperature on the rheology and structure of clay suspensions". MarchCOM meeting 2012. Havana, Cuba. Mar 5-9, 2012. Poster.

Hansen, E.L., Hemmen, H., Fonseca, D. M., Coutant, C., Knudsen, K. D., Plivelic, T. S., Bonn, D., Fossum ,J. O.: "Swelling transition of a clay induced by heating". International workshop on Soft Matter and Complex Flows. Svolvær, Norway. May 22-25, 2012.Poster.

Rude, L.H., Hino, S., Hauback, B.C., Skibsted, J., Jensen, T.R.: Preparation and characterization of fluoride substituted metal borohydrides. International Symposium on Metal-Hydrogen Systems, Kyoto, Japan, October 21-26, 2012. Poster.

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