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SAFESYST

RELEVANT PHYSICAL ASPECTS OF HYDRIDES FOR SYSTEM INTEGRATION AND SAFETY

Schlussbericht

Ausgearbeitet durch

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Inhaltsverzeichnis

Zusammenfassung

Die Wasserstoff-Speicherung wird als Kernherausforderung für zukünftige Anwendungen für Wasserstoff als Energieträger gesehen. Die Speicherung in Festkörpern - speziell komplexen Hydriden - verspricht höchste Energiedichten. Diese hochreaktiven Materialien können jedoch potentiell gesundheitsschädigend sein. Spezifisch die Klasse der Borhydride kann Diboran emittieren, welches nicht nur zum Verlust der Funktionalität sondern auch eine Gefahr für die Umwelt darstellt. Die Reaktion dieser Materialien mit Wasser und Sauerstoff als potentielle Interaktionspartner bei Atmosphärenexposition wurde untersucht, um Effekte der Passivierung und Reaktionsprodukte im Rahmen des Projektes SafeSyst zu ermitteln. Dies bildet einen Grundstein zur Lagebeurteilung über die Reaktion dieser Materialien im Umgebungskontakt. Als zusätzlicher Aspekt wurde die Diboran-Emission bei der thermischen Zersetzung von Borhydriden untersucht. Dies mit dem Ziel, den Mechanismus zu verstehen und Wege zu finden um dies zu unterbinden.

Die Reaktivität von Borhydriden zeigte sich unerwartet unreaktiv bezüglich Sauerstoff-Exposition, jedoch eine höhere Reaktivität bezüglich H_2O. Die Reaktion mit O_2 führt zu einer passivierenden Schicht, die sich rein auf die Oberfläche beschränkt. Aus diesen Ergebnissen entstand eine internationale Zusammenarbeit, in welcher der Desorptionsmechanismus von AlH_3 fruchtbar erklärt werden konnte.

Es wurde festgestellt, dass bei Diboran nur bei hohen Temperaturen thermisch zersetzt. Somit steht dies im Konflikt zu den Bestrebungen einer tiefen Desorptionstemperatur und muss katalytisch zersetzt werden. Die Wechselwirkung mit Oxiden führte zu einer wesentlichen Reduktion der Diboran-Emissionen bei tiefen Temperaturen, eines der Projektziele. Auf der anderen Seite steht die künstliche Erhöhung der Diboran-Emissionen über ZnCl als notwendiges Schlüsselelement zur künstlichen Synthese von Borhydriden heraus, welche bisher nur nasschemisch erzeugt werden konnten und jetzt direkt aus den Elementen hergestellt werden kann.

Resumé

Hydrogen as a potential energy carrier poses new opportunities and challenges towards safety. Solid hydrogen storage in complex hydrides offers very high energy density but require profound knowledge of the material properties. They are highly reactive materials and can be potentially hazardous. Assessment of surface reactivity with impurities and air, passivation mechanisms and decomposition by-products where issues currently not addressed and have been investigated in the project. On borohydrides, the release of diborane not only poses a functional barrier through loss of a reaction partner, it poses also a health hazard in potential release to ambient. These aspects where studied in the framework of SafeSyst.

Surface reactivity under exposure to O_2 and H_2O has been extensively studied on Borohydrides as most likely reactive candidates under air exposure. Even the most reactive borohydride ($LiBH_4$) showed a surprisingly low reactivity towards O_2, but a much higher reactivity towards H_2O. Exposure to O2 yields a passivation lay-

er by forming a surface oxide but leaving the bulk intact. Through these works, a successful international collaboration developed where we could investigate and explain the desorption mechanism of AlH_3 fruitfully.

It has been found, that thermal decomposition of Diborane is only promoted at higher temperatures. This is in conflict with the aim of reaching lower desorption temperatures for these materials. The decomposition therefore has to be promoted catalytically. It could be shown that iInteraction with surface oxides substantially reduced diborane emissions, a key goal of the study. Artificially increasing diborane emission by ZnCl on the other hand turned out to be the key element for successful synthesis of borohydrides from the elements, a procedure which demanded wet chemical processing so far. It enables the synthesis of new materials of this class for future investigation.

1. Introduction

Hydrogen is considered one of the most promising future energy carriers. It is to date the only artificially producible energy carrier, which can potentially satisfy and serve our needs for mobility applications. Storage of hydrogen remains one of the strongest challenges in a future hydrogen economy. While fuel cells have progressed considerably, hydrogen production and storage have remained domains with substantial need of fundamental research. The main challenge with hydrogen storage is, that hydrogen offers very high energy density per mass unit, while on a per volume basis it's energy density is very low. Therefore, liquid, pressurized or solid hydrogen storage is the paths pursued for storing large amounts of energy. Liquefied hydrogen is no longer seen as a viable solution for on-board storage. This is mainly due to complexity of the tank as well as the high energy losses associated with liquefaction. Pressurized hydrogen so far is the option of choice as it is close to market and substantial knowhow from compressed natural gas exists that can be transferred. The limits of pressurized hydrogen storage nevertheless are well known and achievable energy density limits are obvious. The specific physical characteristics of hydrogen are such that compression over 700bars does not increase energy density on a system level. To further increase hydrogen storage density and therefore potential range, only solid hydrogen storage has potential to crack this barrier which is a consequence of the properties of hydrogen.

Solid hydrogen storage is well established in form of so called metal hydrides. Hydrogen is adsorbed in the intermetallic matrix at low pressure. The main drawback is the low gravimetric storage density due to the fact that the intermetallic alloy consists of heavy elements. Complex hydrides on the other hand store large quantities of hydrogen in a solid and consist of light elements. Although they exhibit similar pressure and temperature dependence as classic metal hydrides, there are fundamental differences between the two. The hydrogen is not only adsorbed into a host lattice, it participates in the bonding of the material and therefore, adsorption and desorption can be seen as forming and breaking molecules rather than an adsorption in a sponge where the host material does not change significantly.

The appealing advantage of complex hydrides is, that they store almost an order of magnitude more hydrogen per weight than metal hydrides and surpass compressed hydrogen in that respect substantially. They are, from an energy density point-of-view, close to hydrocarbons we seek to replace. But they come with their own set of challenges. Kinetics (how fast can you desorb) and Stability (how much heat do you have to supply for desorption) as well as reversibility (can it be recharged) are still outside of a practical window. Therefore, research is needed to improve these characteristics into a range interesting for application. Destabilizing the material can well bring the former parameters into an interesting range but can also have unwanted side-effects: Only hydrogen should be desorbed on the destabilized material – but this is not trivial to achieve. Especially on the amides and Borohydrides can potentially desorb ammonia or diborane which are potentially harmful to humans or the environment. As Borohydrides show higher potential towards hydrogen storage, focus remained on these materials.

Another issue towards application of these materials is the reaction with reactive ambient atmosphere contributions, namely H_2O and O_2. It is crucial to know, if these reactions are self-limiting by forming a passivation layer or if the reaction proceeds as long as these contributions are present.

These issues, the emission of diborane and it's circumstances, the potential limitation or elimination of diborane as well as the reactivity of Borohydrides with H_2O and O_2 where investigated in this project and substantial progress could be achieved.

2. Project Goals

Work Package 1: Surface Reactivity

Investigation of the surface reactivity of complex hydrides with oxygen, water and hydrogen impurities by means of X-ray photoelectron spectroscopy and mass spectroscopy.

Work Package 2: Thermal decomposition byproducts

Investigation of the thermal desorption products and description of the desorption mechanism on an atomistic level.

Work Package 3 (optional): Thermal conductivity

Thermal transport in complex hydrides, i.e. in the lattice, in grain boundaries and between particles, and in the hydrogen gas phase.

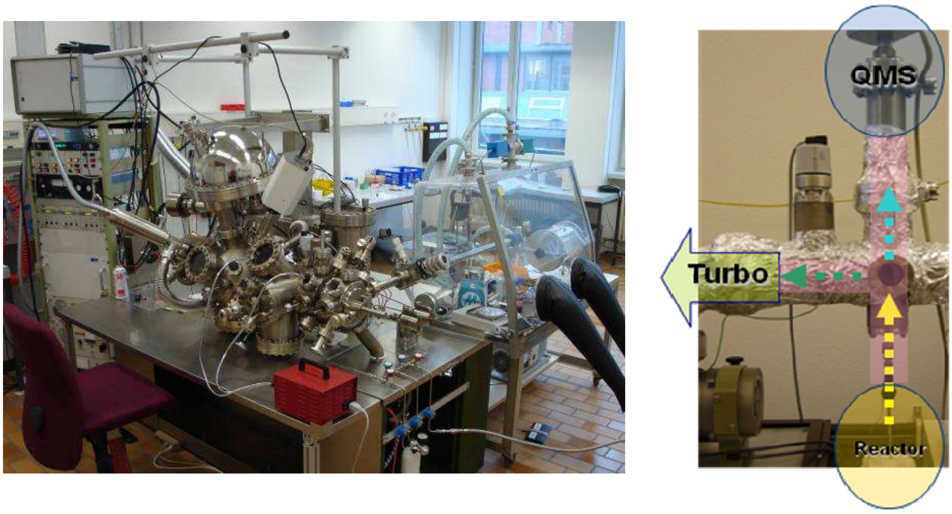
Work Package 4: Dissemination

Dissemination of the results in IEA task 19 (Safety) and IEA task 18 (Demonstration). Collaboration with industry (e.g. SwissRe).

WP3 was defined as optional due to only partial funding of the project. Complementary financial resources could not be secured and therefore WP3 is not actively pursued.

3. Experimental Equipment

The experimental equipment was specifically adapted for the investigations and are represented in Fig. 1.



ESCA (Electron Spectroscopy for Chemical Analysis)

Surface Composition
Surface Chemistry changes due to temperature
Surface Chemistry changes due to gas interaction
Link of gas phase desorption byproducts with surface chemistry

TPD (Temperature Programmed Desorption)

⇒ Mass spectrum as a function of temperature
Gas phase products as a function of temperature
Kinetics
Thermodynamics

Fig. 1 : ESCA allows the surface chemistry and gas phase characterization as a function of temperature and sample preparation without contact with ambient conditions, an absolutely necessary prerequisite to get significant results. Sample temperatures are limited to RT-350℃. TPD allows for the analysis of gas phase desorption products up to higher temperatures (0-650℃) with sample preparation in controlled atmosphere.

4. Results and Discussion

Work Package 1: Surface Reactivity

The reactivity of alkali-borohydrides to exposure with O_2 and H_2O was investigated by controlled dosing of well prepared surfaces insitu. In summary, the samples proved to be substantially more reactive towards H_2O than towards O_2 (Fig. 2). The reaction of $LiBH_4$ with O_2 is confined to the surface. A comparison between the less stable $LiBH_4$ and $NaBH_4$, the former proved to be substantially more reactive (Fig. 3).

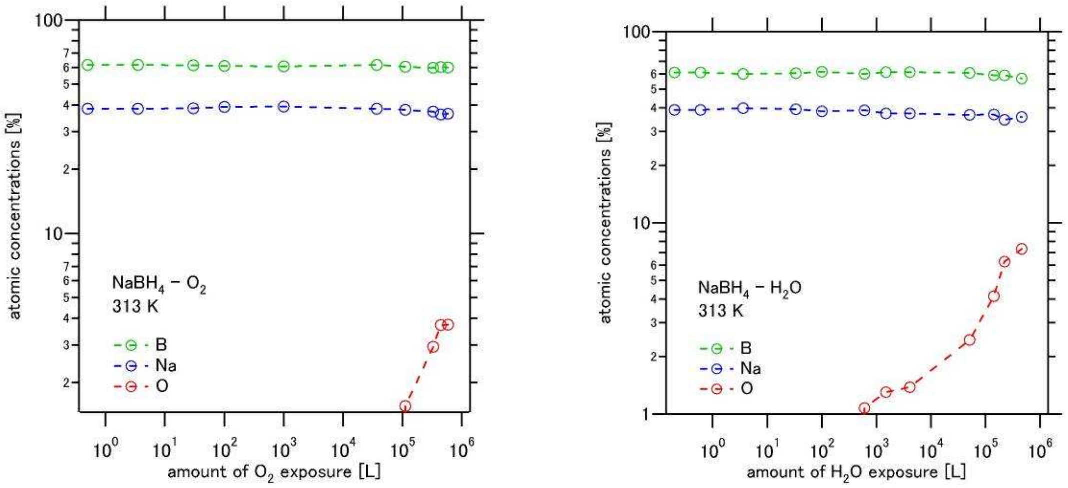


Fig. 2 : Comparison of the reactivity of NaBH4 towards O_2 and H_2O. The reactivity towards H_2O is orders of magnitudes higher. The same trend is observable for all the alkali borohydrides.

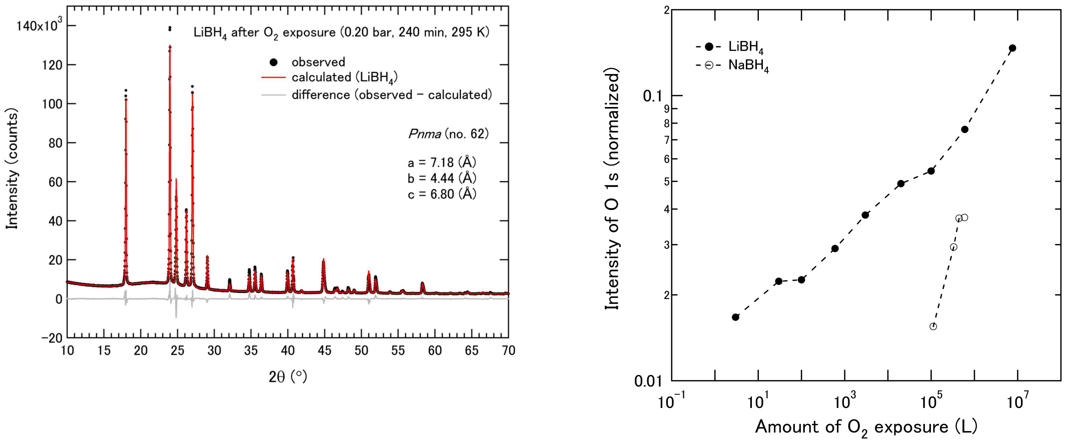
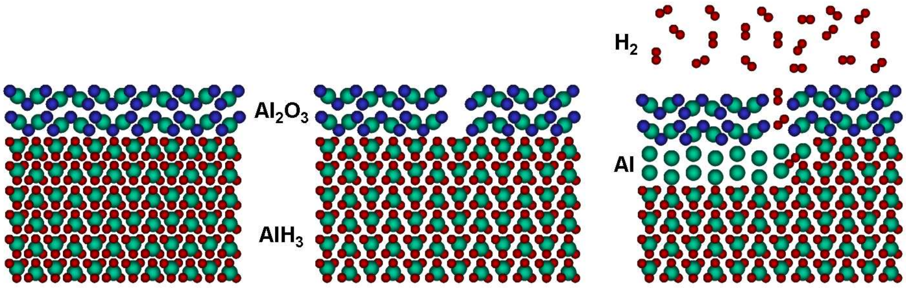


Fig. 3 : (Left) Evolution of the Oxygen signal as measured with ESCA as a function of O_2 -dosing for $LiBH_4$ and $NaBH_4$. The former shows significantly higher reactivity. (Right) The oxidation was proven to be confined to the surface only by XRD, so the bulk remains essentially unchanged

As the main result, we therefore could establish the reactivity of different borohydrides towards the most likely reactive gases to arise in a real world application, namely O_2 and H_2O.

The investigations where extended as planned to the most simple covalent-like hydride. AlH_3 served as a role model for the investigation of oxide layers as a function of temperature. The oxide layer is not a diffusion barrier for hydrogen desorption, it rather acts as a kinetic barrier. These investigations let to a fruitful international collaboration (Fig. 4).



(a) (b) (c)

Fig. 4 : Model of AlH3 surface structure as a function of temperature a.) AlH3 is covered by a natural oxide layer which acts a kinetic barrier for hydrogen desorption b.) upon heating, the oxide layer is developing defects c.) hydrogen desorption starts as the kinetic barrier of the oxide layer is eliminated.

Work Package 2: Thermal decomposition byproducts

The identification of diborane and its byproducts in masspectrometry turned out to be challenging. To get a fingerprint on the masspectrum of diborane, a mixture of ZnCl + $LiBH_4$ was used as a source. By this method, characteristic features of borane and diborane evolution could be established for future measurement (Fig. 5).

The characterization of decomposition byproducts can only be performed qualitatively. The quantitative characterization turned out to be out of range of the current used technology of Quadrupole Massspectrometry. Therefore, only the presence or absence and to some degree the intensity evolution of the emissions can be described, but not the absolute amount of the emissions.

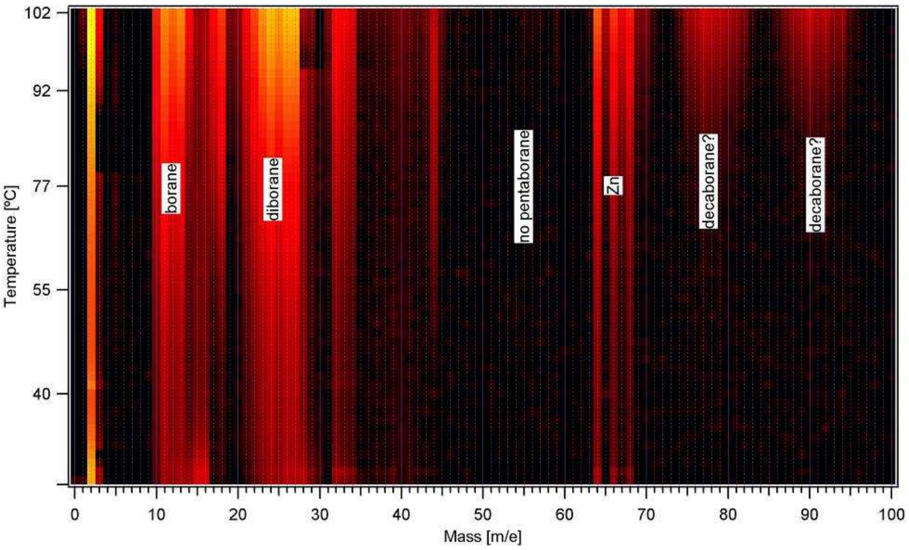


Fig. 5 : Masspectrum of ZnCl + $LiBH_4$ as a diborane source. Characteristic features of borane (BH3) and diborane (B2H6) emissions in the gas phase could be identified for future analysis on the desorption byproducts.

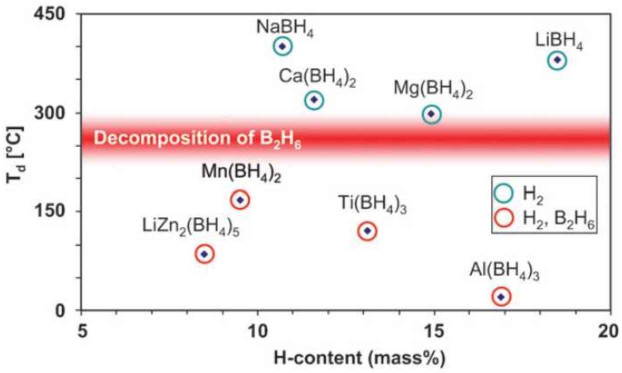


Fig. 6 : Thermal decomposition of diborane. Above approx.. 250℃, diborane is unstable and dissociates thermally. Below this threshold, diborane can be released into the gas phase.

As described in Fig. 6, diborane does dissociate thermally above a 250°C threshold. Below this temperature, thermal decomposition does not take place. To use complex hydrides in applications, lower desorption temperatures are needed and therefore, diborane emission is a crucial issue. Thermal decomposition is no longer sufficient and catalytic decomposition has to be applied.

The (di)borane evolution was investigated mainly on $LiBH_4$ as it is the most unstable of the alkali borohydrides and therefore has the highest potential towards application.$NaBH_4$ and KBH_4 have much higher desorption temperatures and no significant diborane evolution could be measured on these materials. This finding can be mainly attributed to thermal decomposition of diborane in the desorption window, while essentially being to stable at lower temperatures. Diborane emission indeed could be measured around the melting temperature of $LiBH_4$, while essentially dropping to non-significant levels above the melting point, where thermal decomposition of diborane takes place. The unwanted evolution of boranes below and near the melting point could be substantially reduced by the reaction with O_2 (Fig. 7). While the role of oxygen in the process in not yet fully understood, the finding is a substantial step towards the effective suppression of borane emission in the desorption process

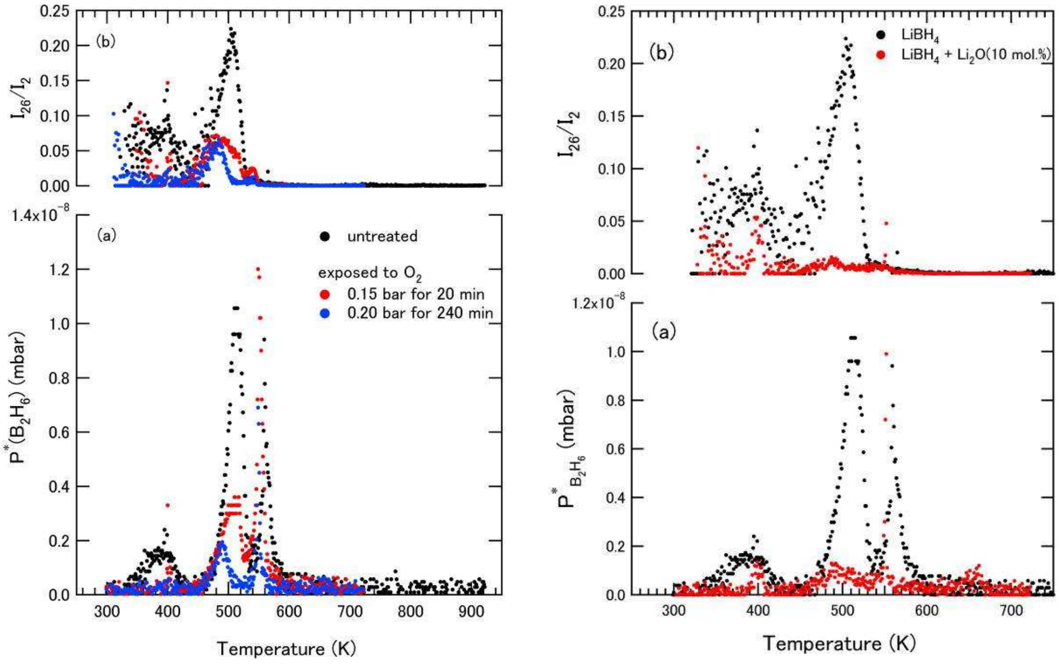


Fig. 7 : (Left) Diborane evolution of $LiBH_4$ as a function of oxygen dosing. The reaction of the surface with O_2 leads to a suppression of diborane evolution into the gas phase. (Right) Effect of admixture of LiO_2 + $LiBH_4$. The presence of oxide substantially reduces the evolution of diborane.

Work Package 4: Dissemination

The IEA Task 19 (Hydrogen Safety) meetings where attended on multiple instances. Although, the possibility for active contribution where limited due to the fact, that we did not participate from the beginning of the task, we profit from the network and the sources of information. IEA Task 19 is disseminating a wealth of information regarding hydrogen safety and Quantitative Risk Assessment.

Results have been extensively published and presented in international journals and conferences.

5. Conclusions

Reactivity of metal borohydrides was established and measured towards H_2O and O_2. While exposure to O_2 resulted in a passivating oxide layer which remains a surface effect, reactivity with H_2O proved to be orders of magnitude stronger.

Emission of diborane mainly occurs below the thermal decomposition window which goes up to approx. 250°C. Therefore, it is not an issue on stable hydrides, but indeed is observed on unstable hydrides. In view of application, reduction of desorption temperature and therefore destabilization is aimed for and in conflict with thermal decomposition of diborane. Catalytic decomposition is therefore the path to follow. In our experiments, interaction with oxides showed a catalytic effect on diborane decomposition, reducing the emissions into the gas phase substantially.

Forced diborane evolution for synthesis of novel borohydrides on the other hand proved to be the key step towards synthesis from the elements. By this process, novel hydrides are getting well into reach which where formerly unavailable for study.

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7. National and International Collaborations

Ch. Zwicky, Abt. 137, EMPA Materials Sciences & Technology dübendorf, Schweiz

K. Ikeda, S. Orimo, Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Dr. M. Fichtner, Institute of Nanotechnology, Karlsruhe Institute of Technology, Germany.

Prof. R. Bormann, GKSS, Gestacht-Hamburg, Germany

8. Presentations

29.4.2010	***Der Weg des Wasserstoff von der Herstellung bis in den Tank*** M. Bielmann, Talk, Fachtagung Verband Öffentlicher Verkehr (VÖV), St. Gallen, Switzerland
17.-19.08.2010	***Hydrogen sorption mechanisms at various hydrides surfaces*** S. Kato, Talk, EMPA-KIST Workshop, Geoje, South Korea
04. - 08.07.2010	***Breaking the passivation - the road to a solvent free borohydride synthesis*** O. Friedrichs, Poster, First International Conference on Materials for Energy, ENMAT2010, Karlsruhe, Germany
19. - 23.07.2010	***Hydrogen sorption mechanisms at various hydrides surfaces and towards synthetic fuels*** S. Kato, Talk, International Symposium "Metal-Hydrogen Systems. Fundamentals and Applications", Moscow, Russia
24. – 29. 01.2010	***Roles of surface oxide layer in hydrogen desorption processes*** S. Kato, Talk, 4th International Symposium Hydrogen & Energy, Hotel Hirschen, Wildhaus, Switzerland
24. – 29. 01.2010	***Diborane - The key to reversible hydrogen storage*** O. Friedrichs, Talk, 4th International Symposium Hydrogen & Energy, Hotel Hirschen, Wildhaus, Switzerland
30.11. - 04.12.2009	***Roles of surface oxide llayer in hydrogen desorpttiion processes by*** AlH_3 ***and*** $LiBH_4$ S. Kato, Poster, MRS fall meeting, Boston, USA
12.-17.07.2009	***Impact of the surface oxidation of*** $LiBH_4$ ***on the*** H_2 ***desorption processes*** S. Kato, Poster, Gordon Conference , Barga (Lucca) Italy
12.-17.07.2009	***Impact of the surface oxidation of*** $LiBH_4$ ***on the*** H_2 ***desorption processes*** S. Kato, Poster, Gordon Conference , Barga (Lucca) Italy

2.4.2009	***Diborane evolution from $LiBH_4$, $NaBH_4$ and KBH_4 during desorption*** M. Bielmann, Talk, Hypothesis VIII Conference, Lissabon, Portugal
25. - 30.01.2009	***Impact of the surface oxidation of $LiBH_4$ on the H_2 desorption process'*** S. Kato, Talk, Symposium Hydrogen & Energy, Braunwald, Switzerland
13. 11. 2008	***Surface oxidation of complex hydrides*** Kato, EMPA PhD Students Symposium 2008, EMPA, St. Gallen, Switzerland
24.-28. 06. 2008	***Surface interactions of complex hydride with reactive gas atmosphere'*** S. Kato, Poster, International Symposium on Metal-Hydrogen Systems, MH2008, Reykjavik, Iceland
23.1.2008	***Mass-flow pcT method for characterization of hydrogen storage materials*** M. Bielmann, Talk, 2nd Symposium Hydrogen & Energy, Braunwald, Switzerland
22.1.2008	***Mass Flow Method for the Characterization of Hydrogen Sorption Kinetics'*** S. Kato, Poster, 2nd Symposium Hydrogen & Energy, Hotel Alpenblick Braunwald, Switzerland,
3.08.2007	***Desorption byproducts from $LiBH_4$ under UHV Conditions*** M. Bielmann, Talk, 2nd ESSHS, Univeristy of Ulster, Belfast, Northern Ireland
18. 07. 2007	***Initial activation of hydrogen absorption'*** S. Kato, Talk, Workshop EMPA-FZK, FZK Karlsruhe, Germany
17.4.2007	***Desorption Characteristics and by-products of $LiBH_4$*** M. Bielmann, Talk, Hydrogen2 Network Meeting, Shell Research Center, Amsterdam, Netherlands
16.2.2007	***A short how-to on hydride characterization*** Inauguration Symposium Hydrogen and Energy, Empa Dübendorf