The 2nd symposium "Hydrogen & Energy" is the follows the successful inaugural symposium in February 2007 at Empa. It serves as an information platform of the fundamental science and the frontiers of research in Sciences and Technology of Hydrogen & Energy.

The second symposium consists of invited keynote lectures reviewing the key elements of the hydrogen cycle. The world leading experts present the current research challenges and newest results in invited and contributing talks. Early stage and experienced researchers present their results and the open questions on posters as well as in a one slide presentation.

The conference takes place in the hotel Alpenblick in the beautiful small village Braunwald on 1'256 m (Eggstöcke 2'449 m) above see level in the Swiss mountains. The village is free of traffic, quiet and offers, beside the scientific program, relaxing moments as well as plenty of sport activities.

The number of participants is limited to 120.


Hotel Alpenblick
CH-8784 Braunwald
Tel 055 643 15 44
URL: http://www.alpenblick-braunwald.ch
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Chair: Arndt Remhof

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Chair: B. Chorkendorff
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**Chair:** Tarek Vegge

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ABSTRACTS
HISTORY OF HYDROGEN

Louis Schlapbach
Empa Materials Science and Technology, CH-8600 Dübendorf, Switzerland

1766 Cavendish reports hydrogen to be 7 to 11 times lighter than air
1783 Balloon made of paper and filled with 25 m³ hydrogen gas ascends to nearly 914 meters
1800 Nicholson and Carlisle separate water into oxygen and hydrogen by passing an electric current through it
1820 Cecil carries out experiments using hydrogen as an engine fuel
1839 Sir William Grove constructs a "gas voltaic battery" as the forerunner of modern fuel cells
1861 Kirchhoff and Bunsen analyze the emitted spectrum of the sun and find hydrogen to be the major constituent of the sun
1866 First dynamoelectric generator demonstrated, ends temporarily the development of fuel cells as electricity generators
1874 Jules Verne writes his novel "The Mysterious Island" in which water delivers energy
1898 James Dewar uses regenerative cooling to become the first to statically liquefy hydrogen
1898 Gmüür starts the first industrial hydrogen production in Switzerland
1909 Fritz Haber discovers a process allowing the synthesis of ammonia (NH₃) from the elements hydrogen and nitrogen
1911 Carl Bosch upscales Haber’s synthesis to industrial production scale
1937 The Hindenburg disaster in Lakehurst ends the air applications of hydrogen after 150 years
1955 Justi describes the utilization of hydrogen as an energy carrier
1957 Lift-off of a hydrogen-powered B-57 Canberra jet, showing the potential of hydrogen as aviation fuel
1959 First fuel cell vehicle equipped with alkaline fuel cells delivering a power of 15kW demonstrated
1961 Kirchhoff and Bunsen analyze the emitted spectrum of the sun and find hydrogen to be the major constituent of the sun
1966 First dynamoelectric generator demonstrated, ends temporarily the development of fuel cells as electricity generators
1974 A hydrogen energy concept using properties of hydrogen including non-conventional energy systems developed
1984 Daimler-Benz together with Aral, Dornier, Mannesmann, Thyssen Engineering demonstrates the Mercedes 280 TE hybrid vehicle equipped with a gasoline and hydrogen internal combustion engine
1988 A triple-jet powered Tupolew Tu-154 flies with a liquid hydrogen fueled engine
1993 Uni Geneva presents a hydrogen powered Lawn Mower
1994 Based on a Mercedes-Benz transporter MB-180, NeCar 1 demonstrates 50kW fuel cell combined with a 30 kW electric drive
1998 The 10 Daimler-Benz vehicles in operation since 1984 ran more than 250'000 km
1998 The EU launches CUTE, Clean Urban Transport for Europe
1998 First Hydroxy demo project with 100 W fuel cell for transportation on water

Corresponding author: Louis Schlapbach, email: louis.schlapbach@empa.ch, Tel. (+41) (44) 823 4500
IDENTIFICATION OF REACTIVE SITE FOR DESIGN OF NEW MATERIALS FOR HYDROGEN PRODUCTION

Ib Chorkendorff
NanoDTU, Department of Physics, Technical University of Denmark, DK-2800 Lyngby

As fossil fuel reserves become depleted in the future, alternative energy carriers such as H₂ may become more prominent. H₂ can easily be produced from fossil fuels and can be a primer for a later sustainable and clean production from solar or wind energy if those are coupled to water electrolysis. Unfortunately, the hydrogen evolution reaction is catalyzed most effectively by Pt-group metals which are scarce and expensive. If this scheme is to become viable, new materials are needed. The importance of identifying the active sites is discussed with respect to make new materials both with respect to electro-catalysis but also conventional catalysis.

Results

In the first I will focus on developing new structured electro-catalysis materials for hydrogen evolution by electrolysis. It will be shown how Pt can be modified by less expensive metals to introduce surface alloys with new properties. Here 736 different systems were ranked theoretically by DFT taking not only reactivity, but also the stability towards phase separation and corrosion into account. We have subsequently tested the most promising candidate, the Bi-Pt surface alloy toward the Hydrogen evolution reaction and found it being improved compared to the standard Pt electrode material [1]. In the second part, new materials inspired by biomimetics will be discussed and it will be demonstrated how the detailed atomic structure, measured by STM, and the hydrogen evolution reaction on MoS₂ clusters can be used to identify the reactive site on the edge of the particles [2, 3]. Possibilities for further enhancement of this effect will be discussed and illustrated by some preliminary examples.

If time allows the importance of identifying the active site and the possibilities for enhancing and improving the conventional catalytic methods for hydrogen production through processes related through the steam reforming process [4] will be discussed. Here we will demonstrate on extended single crystals that the detailed atomic structure on the surface has a great potential for enhancing the reactivity of the nanoparticles, if we can control the presence of the reactive centers [5].

Figure 1 showing the volcano behavior of the exchange current and the position of nanoparticulate MoS₂ shown as an insert.

References


Corresponding author: Ib Chorkendorff, email: ibchork@fysik.dtu.dk, Tel. (+45) 4525 3170

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SOLAR HYDROGEN GENERATION FROM WATER

Michael Grätzel
Laboratory of Photonics and Interfaces, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Silicon-doped α-Fe₂O₃ exhibiting a cauliflower-type nanostructure was prepared by atmospheric pressure chemical vapor decomposition. When used in conjunction with surface adsorbed Co(II) ions to promote water oxidation to oxygen photocurrents up to 2.8 mA/cm² was obtained, corresponding to a solar to chemical conversion efficiency of 4.2% in a tandem cell.

Introduction
The cleavage of water into hydrogen and oxygen by visible light remains the Holy Grail of current photochemical research [1]. In contrast to the “brute-force” approach using photovoltaic panels to electrolyze water, these systems employ semiconductor films or particles, which are able to perform the multi-electron transfer reactions involved in the water oxidation and reduction process. Iron oxide (α-Fe₂O₃, or hematite) is especially attractive as a photo-anode due to its abundance, stability and environmental compatibility, as well as suitable band gap and valence band edge position. However, the reported efficiencies of water oxidation at illuminated hematite electrodes are notoriously low. This lecture reports on the use of mesoscopic hematite films that show promising performance as photoanode in a tandem cell that accomplishes the splitting of water by visible light.

Experimental
We have deposited nano-structured α-Fe₂O₃ films on F-doped SnO₂ glass substrates by ultrasonic spray pyrolysis (USP) and chemical vapor deposition at atmospheric pressure (APCVD). The most efficient photoanodes were obtained with silicon doped hematite films prepared by APCVD. Apart from rendering the films conductive the silicon doping strongly influenced by the mesoscopic film morphology [2]. The silicon-doped α-Fe₂O₃ exhibits a cauliflower-type nanostructure as shown in Figure 1 below.

Results
When used in conjunction with surface adsorbed Co(II) ions to promote water oxidation to oxygen photocurrents up 2.8 mA/cm² was obtained. This corresponds to an overall solar to chemical conversion efficiency of 4.2% in a tandem device using a dye sensitized solar cell as a bottom electrode [3]. The incident photon to water oxidation conversion efficiency reaches 50 percent at 380 nm, the photoactivity of the films extending far into the visible beyond 600 nm. A mechanistic model for water photooxidation is presented, involving stepwise accumulation of four holes by two vicinal iron or cobalt surface sites.

Figure 1. Scanning electron microscopy picture of a silicon doped hematite film supported on fluorine doped tin dioxide (FTO) conducting glass. Note the cauliflower-type nanostructure obtained by APCVD. The feature size is about 14 nm.

References

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LARGE SCALE PRODUCTION OF HYDROGEN – CARBON CAPTURE AND STORAGE AS OPTION?

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In view of the future vision of a “hydrogen economy”, gasifying coal and/or reforming natural gas close to suitable carbon dioxide storage options could be a possible interim solution to the long-term goal of emission-free hydrogen generation. The spatial separation of electricity generation into fossil hydrogen production with CO2 capture and dispersed hydrogen-fueled electricity generation has the advantage of zero emission power generation near to consumers (apart from CO2 also other air pollutants). The construction of an adequate infrastructure would be necessary for this proposed path.

Introduction
The location of hydrogen production plants in combination with decoupled electricity generation and the necessary infrastructure are important aspects. In the past, essential criteria for conventional fossil electricity generation were proximity to consumers as well as the location-bound availability of energy carriers. Transport routes have to be kept short in order to avoid losses and thus additional costs. For conceivable fossil hydrogen production with CO2 capture the existence of storage options will play a key role for plant siting. As a rule, carbon dioxide storage options are not located near existing power plants or exploration sites so possibly new power plant locations must be taken into account.

Analysis
The focus of the contribution will be the analysis of potential fossil hydrogen generation options with CO2 capture, suitable storage options and the resulting energy transport tasks for decoupled hydrogen/electricity generation. Different gasification/reforming options with CO2 capture and the resulting hydrogen generation costs will be described and estimated. The contribution identifies promising technologies and cost trends for the next two decades. The technology and cost analyses especially highlight the requirements of the new infrastructure (e.g. CO2 or H2 pipelines) by means of scenario considerations. Stranded investments could be avoided by also using this infrastructure for the long-term shift to hydrogen economy. The analysis will focus in particular on the German energy system.
SOLAR THERMOCHEMICAL PRODUCTION OF HYDROGEN VIA H$_2$O-SPLITTING CYCLES AND DECARBONIZATION PROCESSES

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Solar thermochemical processes for the production of fuels make use of concentrated solar radiation as the energy source of high-temperature process heat. Considered are water-splitting thermochemical cycles based on metal oxide redox reactions at above 2000 K, and reforming/gasification/decomposition processes for the thermal decarbonization of fossil fuels at above 1500 K. A Second-Law analysis indicates the inherent thermodynamic advantage for efficiently storing intermittent solar energy into chemical fuels via high-temperature endothermic processes, and the potential of avoiding greenhouse gas emissions and other pollutants in the production of hydrogen, syngas, and other synthetic fuels.

The research work encompasses fundamental studies on chemical reactor engineering, with emphasis on the analysis of radiation heat transfer in gas-solid reacting flows. Solar reactor prototypes are designed, fabricated, modeled, and tested in a high-flux solar furnace, and further optimized for maximum solar-to-chemical energy conversion efficiency.

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DEEP DONOR STATES IN InVO₄ PHOTO-ANODES FOR SOLAR HYDROGEN PRODUCTION

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Recent work on InVO₄ photo-catalyst powders suggests that this may be a promising photo-anode material for solar water splitting. Thin films of InVO₄ were deposited by spray pyrolysis, and their optical and electrochemical properties were investigated. Electrochemical impedance analysis reveals a high concentration of deep donors in the material. In contrast to earlier reports, the visible light photo-response of this material appears to be caused by optical transitions to these deep donor levels, and not to an intrinsically small bandgap.

Introduction

The direct conversion of solar energy into hydrogen represents an attractive but challenging alternative for photovoltaic solar cells. Several metal oxide semiconductors are able to split water into hydrogen and oxygen upon illumination. While most of the research efforts so far have been focused on binary oxides, such as (doped) TiO₂ and Fe₂O₃, the past few years have shown an increasing interest in ternary and even more complex metal oxides. When dispersed as a powder in an aqueous solution, several of these materials (e.g. InVO₄, InₓNiₓTaO₄, BiVO₄, NaTaO₃, etc.) can evolve oxygen and/or hydrogen. However, with typical evolution rates of 1 to 100 µmole.g⁻¹.h⁻¹, efficiencies are still too low for practical applications. To investigate the relevant materials properties of InVO₄ in more detail, thin dense films were made by spray pyrolysis, and investigated by optical and electrochemical techniques.

Results

The optical absorption spectra reveal a bandgap of 3.2 eV, which seems to contradict earlier reports on visible light absorption by InVO₄ powders (Ye et al., Chem. Phys. Lett. 356 (2002) 221). A detailed electrochemical impedance study reveals a high donor density (6×10¹⁹ cm⁻³) and a very low conductivity (∼3×10⁻⁸ Ω⁻¹cm⁻¹). These observations can be rationalized by the presence of deep donors in the material.

Fig. 1. SEM image of the InVO₄ film (left), and proposed energy diagram indicating the presence of optically active deep donors.

The presence of ionized deep donors in the depletion layer gives rise to an optical transition from the valence band to the donor level, and we believe that this transition is responsible for the visible light photo-activity of InVO₄ powders. At the same time, these deep defects may also act as recombination centers. This illustrates the important, but often underestimated role of ionic defects on the performance of novel photo-catalysts based on complex oxides.

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PERFORMANCE OF THE RES2H2 WIND-HYDROGEN PLANT IN GREECE

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The wind-hydrogen plant of the Centre for Renewable Energy Sources in Keratea, Greece has been in operation for over two years now. It is composed of a 25 kW alkaline electrolyser, a single-stage hydrogen compressor with filling station at 0.22 MPa, and metal hydride tanks with a LaNi5-based alloy for the storage of 3.7 kg hydrogen, all connected to a 500 kW wind turbine. The performance of the plant has been studied under static and dynamic conditions, according to different operational modes. The charging and discharging characteristics of three metal hydride tanks, supplied with electrolytic hydrogen without purification, will be discussed.

Introduction

There are less than a dozen wind-hydrogen demonstration plants in operation worldwide, presenting important differences, either regarding their components, or their control strategy. The lessons learned from the design, construction and operation of such plants are valuable, because the components and interfaces are far from optimized. The wind-hydrogen plant in the wind farm of CRES in Keratea, was constructed in the context of the FP5 European project RES2H2 (ENK5-CT2001-536), and operation started in October 2005.

Results

The electrolysis stack has not been protected by cathodic polarization during these two years of operation, in order to test the corrosion resistance of the activated electrodes, which seems very satisfactory. The electrolyser performance under variable power input will be discussed.

The operation of the metal hydride tanks charged with electrolytic hydrogen containing around 0.2%v. oxygen and saturated with humidity at the operating pressure and temperature of the electrolyser, without further purification, will also be presented. Metal hydride tanks are suitable for wind hydrogen storage under particular conditions and mainly if hot water is available at an adequate temperature, in order to avoid the use of an electrical boiler. Their control in integrated systems is particularly delicate. An example of the pressure and water temperature evolution during the preheating and discharging of three metal hydride tanks is shown in the figure below.

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OXIDATION AND PHOTO-OXIDATION OF WATER ON THE RUTILE TiO$_2$ (110) SURFACE

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A density functional theory (DFT) based method for computing the free energies of electrode / adsorbate / electrolyte systems [1] is generalised from electrolysis to photoelectrolysis. The oxidation and photo-oxidation of water on the rutile TiO$_2$ (110) surface is investigated using DFT calculations.

We first study different oxygen coverages of the surface in contact with H$_2$O and their relative stability as a function of the applied bias and the pH of the electrolyte, and then analyze the reaction mechanisms of the oxidation of water on the surfaces that are stable over a particular range of bias and pH values, according to the thermochemistry of the reactions four elementary electron transfer reactions, and analyze the overpotential needed for the electrolysis and photo-electrolysis of water.

We found that the most difficult step in the splitting of water process is the reaction of an H$_2$O molecule with a vacancy in the surface to form an adsorbed hydroxyl group (OH$^*$). Comparison to experiment [2] shows that the computed overpotential for O$_2$ evolution (0.78 V) is available under the experimental conditions required for both oxygen and hydrogen evolution.

References


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METAL BOROHYDRIDES FOR ENERGY APPLICATIONS
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Various energy applications of metal borohydrides, such as high-density hydrogen storage, advanced neutron shielding, microwave absorption, and lithium super-ionic conduction, will be introduced in the presentation.

Development of hydrogen storage materials is one of indispensable issues for hydrogen energy applications [1-3]. Candidates for the materials are metal borohydrides such as LiBH₄, Mg(BH₄)₂, Ca(BH₄)₂, Y(BH₄)₃ [4-8]; including their intermediate compounds [9-11]. The thermodynamical stabilities of a series of metal borohydrides (M(BH₄)ₙ with M = Li, Na, K, Cu, Mg, Zn, Sc, Zr, and Hf; n = 1-4) were systematically investigated by using both the first-principles studies and hydrogen desorption measurements [12]. The former indicated that the charge transfer from the metal M (or cation M⁺) to the complex anion [BH₄]⁻ is a key feature for the stability of M(BH₄)ₙ, and also that there exists a linear relationship between the calculated heat of formation ΔH of M(BH₄)ₙ and the Pauling electronegativity χₚ of M. The hydrogen desorption temperature T_d of M(BH₄)ₙ determined using gas chromatography was also closely correlated with χₚ; that is, T_d decreases with an increase in the value of χₚ. Therefore, the Pauling electronegativity χₚ of M is an good indicator for appropriately producing/designing the metal borohydrides M(BH₄)_n for various hydrogen energy applications.

Also, microwave irradiation effects on selected metal borohydrides (LiBH₄, NaBH₄, and KBH₄) were investigated for the promotion of hydrogen desorption reactions [13, 14]. By microwave irradiation, LiBH₄ was heated rapidly above 380 K, at which almost all hydrogen was desorbed. The rapid heating of LiBH₄ is related to a structural transition from orthorhombic to hexagonal at 388 K.

Recently, it was newly discovered that the electrical conductivity of LiBH₄ jumped by three orders of magnitude due to the structural transition [15]. The hexagonal phase above 388 K exhibited a high electrical conductivity of the order of 10⁻³ Scm⁻¹. The electrical conductivity in the hexagonal phase is due to the Li super-ionic conduction. The phenomena will lead to the developments of “solid-state hydride electrolytes” for high-safety lithium ion battery.

References

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CHALLENGES IN THE DEVELOPMENT OF COMPLEX HYDRIDE BASED SYSTEMS FOR REVERSIBLE HYDROGEN STORAGE

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An overview will be given on complex hydride systems which are currently investigated for reversible hydrogen storage. The state-of-the art will be presented for single compounds and combined systems. Setbacks in the development will be outlined, and challenges and opportunities for the future will be discussed.

Although the physical limits of solid storage materials promise storage capacities which are much higher than the conventional storage methods only a few systems have been identified so far which have the potential of meeting the international targets for mobile hydrogen storage (see Fig. 1).

![Fig. 1 Average H-H distances and volumetric storage densities of gaseous (pressurized) hydrogen, liquid hydrogen, and the physical limit of hydrogen in a metal lattice according to the Westlake criterion [1].](image)

Currently there is only one complex hydride compound which seems to have potential to meet the requirements of a technical application [2,3]. Mg(BH₄)₂ has a high H content of 14.9 wt.% H and thermodynamic properties of a room temperature storage material. However, first results indicate that there are problems with the reversibility of the compound at moderate conditions.

The concept of combined systems based on a solid state reaction between a complex hydride and a binary hydride offers the potential of achieving high capacities and low working temperatures. However, not all of the seemingly interesting reactions are practicable because a stepwise reaction may lead to a situation where the calculated overall thermodynamic parameters do not describe the real behaviour of the system [4].

Moreover, there are high kinetic barriers involved in the transformations of such a system. For higher reaction rates a fast and mobile species might be beneficial for the materials transport. But, if such an intermediate is volatile at the operating conditions, this may also be detrimental for the fuel cell and the storage capacity in case the species is desorbed together with the hydrogen.

References


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HYDROGEN STORAGE IN METAL NANOPARTICLES: A NOVEL NANOPLASMONIC HYDROGEN SENSING SCHEME

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Introduction
Localized Surface Plasmon Resonances (LSPR) are collective excitations of conduction electrons in a metal nanoparticle. For an extended surface the surface plasmon resonance energy is determined by the electron structure. For a sufficiently small particle (typically less than a few hundred nm) the plasmon energy depends also on the particle size and shape as well as on its dielectric environment. We have recently systematically characterized the plasmonic properties of supported nanodisk arrays of the transition metals Pt and Pd, fabricated by Hole-Mask Colloidal Lithography [1], over a large size and spectral range (UV-vis-NIR). Spectrally tunable LSPR with cross sections comparable to the “classic” plasmonic materials Au and Ag were found [2].

Experimental
With Pd as model system, we demonstrate a novel plasmonic sensing principle, based on the spectral shift caused by the change in the bulk electronic properties of the particle when a new atom (in this case hydrogen) enters the lattice. Specifically, we use the LSPR as a very sensitive, non-destructive and real-time, remote optical probe to study hydrogen storage in Pd nanodisks in solid solution (α-phase) and metal hydride (β-phase).

Results
Isotherms obeying Sievert’s law were observed in the α-phase region and a typical hysteresis upon charging and discharging with two plateau pressures of 18 torr and 7.5torr, respectively, were observed for the α+β phase coexistence region. A simple model, where the spectral LSPR shift, as well as the change in extinction, were approximated by a linear dependence on the hydrogen content for the α, the α+β and the β phase regimes, could successfully produce p-C isotherms from the LSPR data [3]. The agreement with literature for the bulk Pd-H system is excellent. These results provide a valuable novel experimental approach for studying hydrogen storage materials and open up a novel route towards ultra sensitive optical hydrogen sensors.

References

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NOVEL RESULTS IN HYDROGEN STORAGE AS HYDROGEN CLATHRATE HYDRATES

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It has been discovered that cyclopentane is a significantly better promoter than tetrahydrofuran to stabilize structure sII of hydrogen clathrate hydrate. In addition, promoters were found to stabilize structure sH. This structure is supposed to have a larger storage capacity for hydrogen. Finally, kinetic aspects of the uptake and release of hydrogen in structure sII was studied.

Introduction

In our earlier work [1], we discovered that tetrahydrofuran (THF) is able to stabilize structure sII of hydrogen clathrate hydrate at mild conditions, with as a result that it was recognized as a potential storage material for hydrogen. Additional research did learn that cyclopentane (CP) is an even better promoter than THF for structure sII. Also, for the first time, we were able to find promoters to stabilize structure sH, which structure is supposed to have a higher storage capacity for hydrogen. A major issue are various kinetic aspects that govern the uptake, release and the rapid formation of the material in large quantities.

Experimental

To test the applicability of the new promoters for both structures sII and sH, high-pressure phase equilibrium experiments were conducted. For the kinetic studies a new facility was build.

Results

It was established that CP is a significantly better promoter than THF to stabilize structure sII of hydrogen clathrate hydrate. At a temperature of 281 K an equilibrium pressure as low as of 2 MPa turned out to be feasible. Neutron scattering experiments are in progress to determine the hydrogen storage capacity of this material. Among others, methylcyclohexane (MCH) was found to be able to stabilize structure sH, which structure should have a higher storage capacity for hydrogen. Unfortunately, the equilibrium pressures at ambient temperature are in the range of 50 – 70 MPa, which is too high for a practical material [2]. Finally, we studied the kinetics of hydrogen uptake and release in structure sII. It was found that both processes are completely reversible [3]. A spray technique proved that the solid material easily can be produced in large amounts.

References


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LOW TEMPERATURE RAMAN SPECTROSCOPY OF LiBH₄ AND LiBD₄

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With theoretical 18 mass % hydrogen storage capacity LiBH₄ belongs to the metal hydrides with the largest gravimetric and also volumetric hydrogen storage density. Yet, automotive applications also require favorable thermodynamic and kinetic properties which are closely related to the bonding of hydrogen in the compound. Vibrational spectroscopy is particularly suited to study hydrogen bonds, since the light mass of hydrogen generates high vibrational frequencies and the isotope effect on substitution of deuterium for hydrogen is the largest of any element [1,2]. We report an extensive Raman scattering study of LiBH₄ and LiBD₄ for temperatures from 5 to 300 K.

Introduction
A previous study was limited to temperatures at and above room temperature [3] where many of the Raman lines are weak or even invisible.

Results
The experimental results are compared to theoretical values obtained from a density functional calculation within the generalized gradient approximation. The factor group analysis for the orthorhombic Pnma structure reveals 36 Raman active modes, of which 18 are external vibrations and the second half correspond to internal (stretching and bending) modes. Up to 24 of these modes have been observed and assigned to the symmetry species. An astonishingly good agreement between experiment and theory is found for most of the phonon frequencies. The temperature dependence of the normalized frequency, linewidth and intensity of the Raman modes shows an anomalous behavior for one of the external modes with B3g symmetry. A fit of the linewidth of this mode including an exponential factor indicates a strong coupling of the mode to the librational motion of the BH₄ tetrahedrons. We anticipate that this mode is related to the structural phase transition from the orthorhombic to the hexagonal phase occurring at about 380 K.

References

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RAMAN SPECTROSCOPY TO PROBE HYDROGEN-DEUTERIUM EXCHANGE REACTIONS IN SODIUM ALANATE.

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NaAlH₄ is the archetypical complex hydride for hydrogen storage. The enormous effect of dopants on the sorption kinetics triggered the investigation of its physical origin. In this paper, a short review of the state of the art is given. To gain further understanding of the involved mechanisms we label the interacting species during the sorption process. This was experimentally realized by hydrogen-deuterium exchange measurements during the decomposition of NaAlH₄ followed by thermogravimetry and Raman spectroscopy. By these experiments we are able to obtain special information on the diffusing species and formation of intermediates. The activation energy of tracer diffusion in NaH is was found to be 0.25 eV. The activation energy of tracer diffusion in Ti-doped NaAlH₄ is estimated to be approximately 0.2 eV. The results are evidence for a vacancy mediated desorption process of NaAlH₄.

Introduction
Doped sodium alanate is the archetypical hydrogen storage material for mobile applications [1]. It decomposes in two steps, releasing theoretically 5.6 mass% hydrogen [2]. To gain an insight into the involved mechanisms we label the interacting species during the sorption process. This is experimentally realized by hydrogen-deuterium exchange measurements during the decomposition of NaAlH₄ followed by thermogravimetry and Raman spectroscopy.

Experimental
A magnetic suspension balance Rubotherm (Bochum, Germany) was used to measure thermodesorption kinetics in hydrogen and deuterium atmosphere, respectively, up to a temperature of 750 K. Raman spectra were obtained in backscattering geometry using a Renishaw Ramascope 2000 (Renishaw plc, Gloucestershire, UK) with a spectral resolution of 1 cm⁻¹.

Results
The diffusion of deuterium in pure solid NaAlH₄ is extremely slow. In liquid phase, exchange of hydrogen as well as diffusion is considerable. In Ti-doped NaAlH₄, exchange of hydrogen and diffusion is possible. The exchange process is coupled to the decomposition of NaAlH₄. In pure solid NaAlH₄, the internal Al-H vibrations are hardly affected by a temperature increase - in contrast to the external Na – AlH₄ vibrations. Ballmilled, Ti-doped NaAl₄ does not show significant differences of the Raman spectrum when compared to the pure compound at room temperature. Changes of the spectra are observed at 50°C. From this we conclude that AlH₃ vacancies in NaAlH₄ are formed during the decomposition process, allowing the transport of metal atoms as well as hydrogen.

References

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We demonstrate the direct, solvent free synthesis of Li[B\textsuperscript{11}D\textsubscript{4}] from the corresponding elements at \(T=350\, ^\circ\text{C}\) and \(p(\text{D}_2) = 180\, \text{bar}\). The reaction is realized by applying the pressurized deuterium to a pre-annealed Li-B mixture. The involved intermediate products and the synthesis of the final products were monitored by in-situ neutron diffraction. The reaction starts with the decomposition of the initial Li-B compound and the formation of LiD at \(200\, ^\circ\text{C}\). At \(350\, ^\circ\text{C}\) LiBD\textsubscript{4} starts to form. At this temperature the reaction to LiBD\textsubscript{4} is not complete, it takes temperatures of more than \(500\, ^\circ\text{C}\) to fully transfer the elements involved to LiBD\textsubscript{4}.

To monitor the synthesis of LiBH\textsubscript{4} from the corresponding elements, we used in-situ neutron diffraction. The experiment was carried out at the focusing diffractometer E6 of the Berlin Neutron Scattering Center (BENSC) of the Hahn – Meitner Institute (HMI) in Berlin, Germany. The diffractometer is equipped with a horizontally and vertically bent monochromator consisting of 105 pyrolytic graphite crystals (20 \times 20 \times 2 \, \text{mm}^3) mounted on a 15 \times 7 matrix leading to a flux of \(5 \times 10^6\, \text{n/cm}^2\text{s}\) at the sample position using neutrons of the wavelength of \(\lambda = 0.24\, \text{nm}\).

We first filled a standard stainless steel sample container with a mixture of ball-milled \textsuperscript{11}B and natural Li, corresponding to the stoichiometry LiB\textsubscript{3} and placed it into a high temperature furnace (HTF). After heat treatment at \(330\, ^\circ\text{C}\) for 60h in inert He atmosphere, the HTF was placed onto the sample stage of the E6 instrument and the sample container was connected to the gas loading system, supplying deuterium (D\textsubscript{2}) at 180 bar. LiBD\textsubscript{4} melts at \(280\, ^\circ\text{C}\), all measurements have been carried out at room temperature, except the one recorded at \(200\, ^\circ\text{C}\).

The intermetallic Li-B compound is characterized by a strong reflection at \(2\theta = 40°\). Above \(200\, ^\circ\text{C}\) the sample absorbs D\textsubscript{2} at large amounts, and LiD is formed. At about \(350\, ^\circ\text{C}\) LiBD\textsubscript{4} can clearly be identified, together with an increasing amount of LiD.

![Fig. 1 Synthesis of LiBD\textsubscript{4}, monitored by neutron powder diffraction](image)

Increasing the temperature to \(500\, ^\circ\text{C}\) leads to a decrease of the LiD-reflection and to a further increase of the LiBD\textsubscript{4} reflections. Higher temperatures and/or more time is necessary to complete the reaction.

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In the present work we investigate the hydrogen sorption mechanism in a MgH$_2$/Nb$_2$O$_5$ composite and analyze why Nb$_2$O$_5$ could strongly improve hydrogen sorption kinetics in magnesium. A detailed microstructural and chemical analysis of the evolution of the additive during the H$_2$ sorption processes allowed us to identify the formation of ternary Mg-Nb-O phases that during migration to the surface produce “pathways” allowing the easy diffusion of hydrogen into the Mg nanocrystals.

**Introduction**

Nano-crystalline MgH$_2$ powders produced by high energy ball milling [1] show a significant progress in the sorption kinetics compared to bulk polycrystalline Mg. The addition of additives, mainly transition metals and oxides, during ball milling of MgH$_2$ introduced also a big improvement in the hydrogen sorption kinetics [2]. Nb$_2$O$_5$ was one of the best additives found. Here we present our results to elucidate the mechanism by which these oxides are improving the kinetics.

**Experimental**

The samples were ball milled-MgH$_2$, additionally milled with 5-10 wt% Nb$_2$O$_5$ as additive. Samples characterization was carried out by XRD, XPS, TEM and XAS. Kinetic sorption measurements were carried out by a volumetric Sievert apparatus.

**Results**

Here we present our results indicating the formation of ternary Mg-Nb-O phases [3] that during migration to the surface produce “pathways” allowing the easy diffusion of hydrogen into the Mg nanocrystals. Hereby we also show the application of Nb$_2$O$_5$-nanoparticles as milling additives [4], by which the milling time could be reduced by more than a factor 200 compared to a system of MgH$_2$ milled with microcrystalline Nb$_2$O$_5$.

![Fig.1. Formation of hydrogen pathways through the MgH$_2$ and the MgO surface oxide layer. Left: original sample. Right: Sample after first desorption.](image)

**References**


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FLOW-pCT METHOD FOR CHARACTERIZATION OF HYDROGEN STORAGE MATERIALS

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In this contribution, the thermodynamic characterization by the so called Flow-pcT is presented for the benchmark material of LaNi5. This method, in contrast to the Sieverts-PCT, is continuous and therefore eliminates this inherent draw back of volumetric characterization methods. The measurement process as well as the data analysis to obtain the Van’t Hoff plot and hence the thermodynamic parameters of the storage material is explained by measurements on LaNi5 as a benchmark due to the well characterized properties of this material. The results match perfectly the literature values for this material of $\Delta H = -32.5$ kJ/molH$_2$, $\Delta S = -115$ kJ/molH$_2$ and and show the validity and quality of the Flow-pcT method.

Introduction

The determination of $\Delta H$ and $\Delta S$ from Van’t Hoff Plots are the usual way for thermodynamical characterization of hydrogen storage materials. There exist a multitude of methods for the construction of van’t Hoff Plots whereas the volumetric Sieverts method is the most frequently applied. This method, consisting of a known reference volume filled with hydrogen which is expanded into the sample cylinder and establishing the amount of hydrogen sorbed from the ideal gas laws - while conceptually apparently simple, suffers from a multitude of complications due to the inherent step-by-step approach of data acquisition which render data analysis complicated and difficult [1]. Data acquisition in a manual system is tedious as each measurement point needs to be recorded individually, involving valve actuation. The flow-pcT method eliminates many draw backs and while conceptually more complicated offers many advantages which are presented in this presentation.

Experimental

The flow-pcT method is based on the concept of exposing the sample to be characterized to a constant flow of hydrogen while recording the pressure and temperature over the sample. While this type of measurement is not in equilibrium by definition, variation of the flow for different measurements an extrapolation of the plateau pressure towards zero-flow e.g. equilibrium pressure is a straight forward process. From the equilibrium pressures at given temperatures, the evaluation of the van’t Hoff plot directly reveals the sought thermodynamic parameters. The schematic concept, the acquisition process and analysis of the data are presented using well-characterized LaNi5 as a benchmark material. The acquisition process is continuous, eliminating user-action for the acquisition of one run and increasing point density by orders of magnitudes hence improving vastly the quality of acquired data.

Results

The process of establishing the thermodynamic parameters is discussed from the raw data measurements to the final results for LaNi5 at different temperatures and flows for desorption experiments. The excellent agreement with tabulated values underlines the quality of this type of measurements.

References


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CALCULATIONS ON HYDROGEN IN NANOSCALE METAL CLUSTERS

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The results of theoretical, DFT calculations on hydrogen in small metal clusters containing mainly aluminum and/or magnesium and, in some cases, also some transition metal will be presented. The results indicate that small MgH2 clusters release hydrogen at a higher temperature than the crystal, unless the clusters are extremely small, with fewer than 5 atoms. The addition of Ni or Zr does not significantly affect the desorption temperature. The results on the Al and Al-H clusters are quite unexpected and promising. As hydrogen is adsorbed, the cluster deforms and opens up so as to accommodate nearly three hydrogen atoms per Al atom, giving about 10% hydrogen by weight. Since the hydrogen atoms bind at surface sites, the binding energy is much stronger than in bulk AlH3, about 0.20 eV per hydrogen atom, close to the target value for hydrogen storage.

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**DFT MODELLING OF NOVEL MATERIALS FOR HYDROGEN STORAGE**

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Quantum chemical computer simulations based on density functional theory (DFT) have shown great potential in the search for novel materials for reversible solid state hydrogen storage. This is particularly true for the high capacity alanate and borohydride systems, which are both difficult to synthesize and characterize experimentally, and require the use of catalysts for practical applications. As of now, many of the fundamental properties, rate limiting processes and catalytic interactions in these materials remains to be understood.

**Introduction**

We present a number of examples illustrating the potential of DFT calculations in the search for better materials for hydrogen storage. The examples range from alloy screening studies using simple model structures to the characterization and prediction of stability at finite temperatures of novel structures and materials.

**Calculations**

Electronic structure calculations are performed using density functional theory in the DACAPTO plane wave basis set [1] and VASP implementations. Lattice dynamics and vibrational free energies are calculated, using the PHONON code, to investigate stability at finite temperatures, and calculations of diffusion rates are based on the NEB method and transition state theory.

**Results**

Close integration of the DFT calculations with experimental techniques, such as quasi-elastic neutron scattering (QENS) and small-angle X-ray scattering (SAXS), is used to provide new insight into the catalytic and nano-scale properties of the materials for hydrogen storage. The role of titanium based catalysts on the reversible de-hydrogenation of NaAlH₄, including hydrogen desorption and diffusion processes is investigated [2], and DFT is used to analyze thermodynamic properties, characterize structures and phase transitions in LiBH₄ [3] and Mg(BH₄)₂ [4].

![Fig. 1. The proposed 704 atoms Fddd structure of \( \beta-Mg(BH_4)_2 \) [3].](image)

Results on indirect storage of hydrogen in the form of ammonia stored in metal ammines, e.g. Mg(NH₃)₆Cl₂ and Ca(NH₃)₈Cl₂ will also be presented [5].

**References**


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ABOUT THE STABILITY OF COMPLEX HYDRIDES

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The stability of a metal hydride is defined as the difference between the enthalpy of the hydride and the enthalpy of the metal or intermetallic compound. This difference is considered to be the same for the hydrogen absorption and desorption reaction, neglecting inelastic effects causing a hysteresis. For complex hydrides the enthalpy of formation is given by the enthalpy of the complex hydride, while the hydrogen desorption takes place via intermediate products leading to an enthalpy for desorption which is significantly smaller than the enthalpy of formation.

Introduction

The stability of complex hydrides is investigated based on the enthalpy of formation of the elemental hydrides and the intermetallic compounds involved in the reaction. The equilibrium hydrogen pressure for the absorption and desorption reaction is calculated.

Theory and Model

The mechanism for the hydrogen absorption and desorption in complex hydrides is not known yet. In the conventional view the complex hydride with a general formula of $M^x[TH_4]_x$ ($M = Li, Na, Mg, Ca...; T = Al, B, N$ and $x$ is the stoichiometry) releases H- to form MH$x + x·TH_3$ [1]. The stability of the AlH$_3$ < BH$_3$ < NH$_3$, therefore, alanates decompose into hydrogen and aluminum while boranates tend to liberate beside hydrogen also B$_2$H$_6$ and the ammonium spontaneously decomposes into NH$_3$. Therefore, the thermodynamics i.e. stability and kinetics is calculated based on the intermediate products identified.

Results

The stability of the TH$_x^-$ is determined by the localization of the electron on the T-atom [2]. As a consequence the stability of the complex hydride strongly depends on the electronegativity of the cation. However, this approach is only able to describe the stability of the forth hydrogen atom in the anion.

The stability of the neutral and “hypothetical” TH$_3$ is also determining the equilibrium pressure of the complex hydride.

Fig. 1. Energy diagram of metal and complex hydrides.

The appearance or the induced creation of intermediate products in the hydrogen desorption reaction is a possibility to destabilise the complex hydrides and to facilitate the reversible hydrogen absorption [3].

References


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SOME APPLICATIONS OF INS AND DFT IN HYDROGEN CONTAINING MATERIALS, THERMODYNAMICS STUDY OF THE STRUCTURAL AND DYNAMICAL PROPERTIES

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The neutron is an ideal probe for the study of hydrogenous materials [1]. Neutrons are scattered by atomic nuclei. All molecular vibrations are neutron-active because the nuclear interactions are not subject to dipole or polarisability selection rules. All vibrations are in principle, observable. Because the neutron has a mass, it also allows the sampling of the vibrations in the Brillouin zone. The intensity of the vibrational modes is proportional to the amplitude of motion of the atoms in the solid; this combined with the lack of selection rules makes the comparison of calculated spectra with experimental straightforward [2]. All these characteristics combined make INSS (Inelastic Neutron Scattering Spectroscopy) an ideal test bed for the applicability of quantum mechanical ab initio calculations.

In the solid it is possible to take into consideration quantum effects by means of the quasi-harmonic lattice dynamics approximation. The quantity to be minimised is the Helmholtz free energy, which includes the zero point motion as well as thermal effects. This approximation is considered to be valid over a wide range of temperatures, but it is especially valid up to room temperature [3]. We tested different functional in DFT calculations and found that in the case of the whole series of simple metal hydrides (LiH ... CsH) the better structural and dynamical agreement, for calculations including thermal effects was when using LDA functionals rather that the most widely “trusted” GGA functionals. Further studies demonstrated that the same effect is observed on other systems, most notably in polyethylene [4]. In this talk I’ll address the capabilities of INS spectroscopy and the correspondence with ab initio dynamical calculations.

References


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MAY TITANIUM BE A GOOD CATALYST FOR LiBH$_4$ SYNTHESIS?

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Titanium is known additive that can catalyze synthesis and decomposition of sodium alanate (NaAlH$_4$). For lithium borohydride (LiBH$_4$) such additive is not known. While Ti affects decomposition of lithium borohydride it has no effect on synthesis of this compound. We have analyzed interaction of Ti with both compounds. Incorporation of Ti into the bulk of NaAlH$_4$ may be exothermic for high oxidation states of Ti cation, unlike for LiBH$_4$.

Introduction
The catalytic effect of metal additives on kinetics of hydrogen adsorption/desorption is not understood on the microscopic level, even for sodium alanate. In particular, it is still under debate whether Ti affects only the surface or it also influences stability of the bulk NaAlH$_4$. Several theoretical studies provide insight into interaction of Ti atoms with NaAlH$_4$. No method that facilitates LiBH$_4$ as a practical hydrogen storage media is known.

Method
Periodic density functional (DFT) method and thermodynamic considerations were used to study formation energies of Ti related defects in complex hydrides and the electronic structure modifications related to formation of Ti defects (substitutions and interstitials) in the bulk and on the surface.

Results
We have shown that description of Ti incorporation process in/on NaAlH$_4$ and LiBH$_4$ shall include not only neutral atoms, but account for the charge transfer effects that was omitted in the literature. Higher oxidation states of Ti are unstable one the surface of sodium alanate and lithium borohydride but under certain conditions Ti$^{n+}$ cations are stable in the bulk of NaAlH$_4$. Ti$^{n+}$ cations incorporated into alanate locally modify charges on the AlH$_4$ groups. For Ti inside NaAlH$_4$ bonding states to the closest Al are observed, while in LiBH$_4$ Ti orbitals are localized exclusively on Ti, see Fig. 1.

![Fig. 1. Local density of states (dashed line) projected on B in LiBH$_4$ (a) and Al in NaAlH$_4$ (b) ions that are closest to interstitial Ti. The LDOS for undoped samples are shown by thick solid lines and LDOS projected on Ti are shown by thin solid lines for the reference. The insert shows the real space projection of neutral Ti gap states. Smaller (blue) sphere is for Ti, larger (gray) for Al.](image)

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ALKALINE METAL-BORON SYSTEMS: FIRST PRINCIPLES CALCULATIONS.

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First-principles calculations of the electronic structure of MₐB₃ (M = Li, Na, K) has been performed to investigate the stability of interstitial metal atoms dissolved in rhombohedral phase of boron. Lattice distortions and bulk properties are analysed comparing the action induced by different alkaline metals. Surface processes at low coverage are also investigated to elucidate the mechanism of reaction metal-boron. The present study represents the first step towards a comprehensive description of ternary phase diagram metal/boron/hydrogen.

Introduction
The importance of alkaline metal/boron systems has recently rewined due to the enormous interest in light metal borohydrides as suitable compounds for hydrogen storage. In order to describe and hence drive the mechanism of the solid state reaction between a metal and boron, it is quite crucial to clarify the chemical nature of the interactions involved at atomistic level.

Computational method
Wave-function based approach is employed based on cluster model of metal-boron systems at CAS-SCF and MP2 level of theory. Periodic cell calculations are run at density functional theory (DFT) level using the generalised gradient approximation (GGA) with the PBE functional and a free-energy functional at a finite electron temperature, as implemented in CPMD code.

Results
The energy-volume curve calculated at different compositions can help to elucidate the chemical action of metal atoms on boron structure. The lattice distortion and the reticular expansion induced by interstitial metal atoms indeed clarify the chemical nature of the bond formed into the bulk. Surface processes at the interface metal/boron represent preliminary steps to alloy and compound formation. Thus the potential energy surface (PES) is calculated at low coverage.

References

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OXYGEN EVOLUTION REACTION IN DIFFERENT CONTEXTS

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We perform density functional theory (DFT) calculations to analyze the electrochemical water-splitting process producing molecular oxygen (O₂) and hydrogen (H₂). We investigate the trends in the electrocatalytic properties of (110) surfaces of rutile-type oxides (RuO₂, IrO₂, PtO₂, MnO₂ and TiO₂). The oxide anodes show lower O₂-evolving over-potentials than metal anodes, due to weak O binding but strong hydroxyl (HO*) binding on the surface. The binding energies of O, HO, and HOO on the (110) surfaces fulfill universal linear relations similar to those found on metal surfaces. Furthermore we compare the oxides to the Mn-cluster from photosystem II. We find that the thermo-chemical features of the catalysts can be directly compared. We identify the optimal binding of the oxidation states and find that the Mn-cluster in photosystem II is close to optimal, even better than the best inorganic surfaces RuO₂ and MnO₂.

Introduction

Electrolysis of water is a route to produce pure CO-free hydrogen and dependent on the energy source possibly non-polluting. However, the reaction is in general related with a substantial overpotential and an effective catalyst for this reaction is therefore needed. We investigate the origin of the over-potential for elemental metal oxide surfaces applying density functional theory calculations [1]. In biology oxygen evolution is one of the steps in photosynthesis where evolution oxygen is a byproduct and a necessary condition for all higher life forms. We compare the biological enzyme to the inorganic catalysts [2]. The best known anode catalysts are RuO₂ known to show the lowest overpotential. In nature the same reaction is catalyzed by a Mn-cluster that has been conserved throughout history of evolution.

Method

We consider the reaction:

\[ 2\text{H}_2\text{O} \rightarrow \text{HO}^* + \text{H}_2\text{O} + \text{H}^- + \text{e}^- \rightarrow \text{O}^* + \text{H}_2\text{O} + 2\text{H}^+ + 2\text{e}^- \]
\[ \rightarrow \text{HOO}^* + 3\text{H}^+ + 3\text{e}^- \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \]

The * represents an active surface site. We are only considering reaction steps involving charge transfer, which depend directly on the applied potential. We consider a process where oxygen molecules are formed by an associative mechanism on the anode via a surface HOO* intermediate. We find that the overpotential of the rutile oxides can be described by the oxygen binding at the surface see, Fig 1

References

LITHIUM AND SODIUM AMIDOBORANES – NEW HIGH CAPACITY HYDROGEN STORAGE MATERIALS

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The safe and efficient storage of hydrogen is widely recognized as one of the key technological challenges in the transition towards a hydrogen-based energy economy.¹⁻² Ammonia borane, NH₃BH₃, is one of a number of condensed phase compounds that have received significant attention because of its reported release of ~12wt% hydrogen at moderate temperatures (~150°C). However, the hydrogen purity suffers from the release of trace quantities of borazine. In this letter, we report that the related alkali metal amidoboranes, LiNH₂BH₃ and NaNH₂BH₃, release ~10.9wt% and ~7.5wt% hydrogen, respectively, at significantly lower temperatures (~90°C) with no borazine emission.

Introduction

We report the synthesis and structure of lithium amidoborane (LiNH₂BH₃) and sodium amidoborane (NaNH₂BH₃) and report that they show substantially different and improved dehydrogenation characteristics with respect to ammonia borane itself.

Experimental

LiH, NaH and NH₃BH₃ (95%, 95% and above 90%, respectively), were used without further purification in hydride/AB molar ratio of 1:1 and were ball-milled on a Retsch PM400 planetary mill at 200rpm. Graphite was added to the mixture to enhance ball milling efficiency.

Results

Alkali metal amidoboranes, LiNH₂BH₃ and NaNH₂BH₃, satisfy a number of the principal criteria demanded for hydrogen storage media. LiNH₂BH₃ and NaNH₂BH₃ provide high gravimetric weight percents (10.9wt% and 7.5wt%, respectively) of hydrogen at easily accessible dehydrogenation temperatures (ca. 90°C) without unwanted by-products, borazine. These materials offer significant advantages over their parent compound, ammonia borane. Alkali metal amidoboranes are also environmentally harmless, non-flammable, non-explosive and stable solids at room temperatures and pressures.

Fig. 1. The Structure of LiNH₂BH₃ and NaNH₂BH₃.

References


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HYDROGENOGRAPHY: FROM Pd TO COMPLEX METAL HYDRIDES

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We have demonstrated that the change in optical properties on hydrogenation make metal hydrides perfectly suited for a thin film combinatorial search for new hydrogen storage materials [1]. Using Hydrogenography, we measure simultaneously the enthalpy of hydride formation of thousands of materials on a single thin film wafer. From extrapolation of the optically measured Van’t Hoff plots, we obtain the entropy of formation. Using very thin layers of Pd we reproduce the Van’t Hoff relation both in absorption and desorption, the latter data in full accordance with previous literature bulk data [2]. Comparing these data with Mg-Ti-H films (which is a mix of coherently ordered fcc MgH2 and TiH2) we find an anomalously large hysteresis. The steps towards the formation of thin film alanates is a formidable challenge. For this purpose we set up a dedicated thin film sputtering and analysis system. We will discuss our first attempts to form alanate thin films by hydrogenation of co-deposited NaH, Al, Ti thin films.

References


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HYDRIDE FORMATION IN MECHANICALLY ACTIVATED Mg-BASED SYSTEMS

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We present results for Mg-based powder mixtures which were ball milled (i) at room temperature in an inert Ar atmosphere, (ii) at liquid nitrogen temperature (cryomilling), and (iii) at room temperature in a reactive H₂ atmosphere (reactive milling). The structural and microstructural evolution of the powders was followed by powder diffraction analysis. Results on the formation of Mg-based hydrides upon reactive milling or during conventional hydrogenation of ball milled or cryomilled powders in a Sievert-type apparatus, are presented. The effect of the different processing conditions, e.g. milling temperature and milling atmosphere, on the phase-selection process is discussed.

Introduction

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 which results in an improved H-sorption kinetics [1]. On the other hand, upon ball milling, elements and/or compounds are mixed at an atomic scale and the resulting extended solid solubility between metals, allows the production of metastable alloys, which might show interesting hydrogen storage properties [2].

Experimental

Powder mixtures with composition Mg₆₇Co₃₃, Mg₆₇Fe₃₃, or (Mg₀.₈Ti₀.₂)₆₇Ni₃₃ were ball milled in Ar using either a Fritsch P6 planetary ball mill or a SPEX 6750 Freezer/Mill. The latter allows milling to be carried out at liquid nitrogen temperature (cryomilling). For the planetary mill, a modified vial equipped with a valve allowed milling also in a H₂ atmosphere at 5.5 bar. The powders ball milled in Ar were subsequently hydrogenated in a Sievert-type apparatus.

Results

Formation of Mg₂CoH₅ and Mg₂FeH₆ is achieved by reactive milling in H₂ or by hydrogenating, at a relatively low temperature and pressure, the powders ball milled in Ar. In both cases, the compounds form directly from the elements, with no indication of formation of MgH₂ as a precursor. Cryomilling has been found effective for reducing the particle size and, in turn, for enhancing the kinetics of phase formation. In addition, cryomilling of Mg-Ti-Ni powders results in the formation of a composite consisting of Mg₂Ni and a Ti-containing amorphous phase. For such a composite, absorption in 12 bar H₂ occurs at relatively low temperatures: 2.5 wt.% and 1.9 wt.% H₂ are absorbed at 100 °C and 150 °C, respectively.

References


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The thermal decomposition steps of Mg(BH₄)₂, which has 14.9 mass% hydrogen capacity, were investigated under He flow and various hydrogen pressures up to 50 bar. In a He flow, the main decomposition of Mg(BH₄)₂ occurs between 250 and 410 °C until 12.1 mass% is lost, with three main peaks of hydrogen desorption. In the first decomposition step the crystalline phase of Mg(BH₄)₂ disappears while a small amount of Mg is detected in the XRD profile. However, the major part of the sample is in an amorphous state. After the second step, crystalline MgH₂ is observed together with Mg phase. The third step of hydrogen desorption corresponds to the decomposition of MgH₂ and Mg is the only crystalline phase observed by XRD measurement after heating to 410 °C. Moreover, even after the decomposition of MgH₂, further hydrogen evolution of 1.4 mass% is observed from 410 °C to 550 °C. Only after this hydrogen desorption, MgB₂ appears in the XRD spectra of the sample. These results indicate that amorphous, hydrogen containing boron compounds take part as intermediates in the reaction. Combined TG - DTA - MS data suggest that the decomposition scheme shows five distinct transformation steps and it appears to be more complex than the simple scheme suggested in earlier publications [1]. Decomposition under static hydrogen pressure up to 50 bar, shifts the decomposition steps to higher temperature, however the decomposition scheme seems to be essentially the same and final stable compound (at 500°C) of Mg(BH₄)₂ is MgB₂ in both inert and hydrogen gas atmosphere.

References

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STABILITY AND REVERSIBILITY OF LiBH₄

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The stability of LiBH₄ was investigated by pcT- (pressure, concentration, Temperature) measurements under constant hydrogen flows and extrapolated to equilibrium. According to the van ‘t Hoff equation the following thermodynamic parameters are determined for the desorption: enthalpy of reaction $\Delta H = 74$ kJ mol⁻¹ H₂ and entropy of reaction $\Delta S = 115$ J K⁻¹ mol⁻¹ H₂. LiBH₄ decomposes to LiH + B + 3/2 H₂ and can theoretically release 13.9 wt% of hydrogen for this reaction. It is shown that the reaction can be reversed at a temperature of 600 °C and at a pressure of 155 bar. The formation of LiBH₄ was confirmed by XRD (X-Ray Diffraction).

Introduction

In this work the enthalpy $\Delta H$ and entropy $\Delta S$ of reaction of the desorption of LiBH₄ were determined by pcT-measurements. The logarithm of the equilibrium pressure $p_{eq}$ divided by standard pressure $p_0 = 1.01325$ bar as a function of the inverse temperature is represented in a van ‘t Hoff plot and $\Delta H$ and $\Delta S$ are determined according to the van ‘t Hoff equation:

$$\ln \left( \frac{p_{eq}}{p_0} \right) = \frac{\Delta H}{R} \cdot \frac{1}{T} - \frac{\Delta S}{R}$$

The slope of the straight line is proportional to $\Delta H$ the axis intercept is proportional to $\Delta S$.

Experimental

For the pcT measurements 250 mg of LiBH₄ from Sigma-Aldrich were heated to temperatures between 400°C and 520°C under a pressure of 20 bar hydrogen. The measurements were performed at different constant hydrogen flows of 0.1, 1 and 2 sccm respectively. The rehydrogenation was made at a pressure of approximately 155 bar H₂ at a temperature of 600 °C for 200 min.

Results

The different plateau pressures for the different temperatures and flows are shown in Fig. 1. Because the plateau pressures depend on the applied flow $\ln(p_{eq}/p_0)$ as a function of the flow is extrapolated to the equilibrium (0 sccm) (red squares). From the van ‘t Hoff equation the following values were found: enthalpy of reaction $\Delta H = 74$ kJ mol⁻¹ H₂ and entropy of reaction $\Delta S = 115$ J K⁻¹ mol⁻¹ H₂.

In the rehydrided material 8.3 wt% of hydrogen was desorbed compared to 10.9 wt% desorbed in the first dehydrogenation.

Fig. 1. Van ‘t Hoff plot of LiBH₄ (desorption) [1]

References

CRYSTAL STRUCTURE OF Ca[BD₄]₂

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Ca[BD₄]₂ with a high gravimetric hydrogen density of 11.5 mass% is among the most promising hydrides for hydrogen storage. The crystal structure of Ca[BD₄]₂ was to a large extent still unknown, with a variety of structures found depending on the synthesis process and temperature of the samples.

Introduction

A room temperature crystal structure of Ca[BD₄]₂ obtained by drying Ca[BD₄]₂·2THF was recently determined and called α-phase [1]. In sample synthesized from MgB₂ by solid gas mechanochemical reaction [2], the room temperature α-phase of Ca[BD₄]₂ phase was found to transform to a unsolved β-phase of Ca[BD₄]₂ at about 130°C [2]. In sample synthesized by wet chemical method [3], coexistence of a unsolved γ-phase with the β-phase from room temperature up to 330°C [4].

Experimental

We have investigated and solved the crystal structure of the β-phase and γ-phase of Ca[BD₄]₂ by combined X-ray and neutron diffraction on a sample synthesized from MgB₂ by mechanochemical reaction and on a sample synthesized by wet chemical method [5]. Experimental results were supported by ab-initio calculations in order to find the optimal structural candidates.

Results

For the determination of the structure of the β-phase, investigation of eight space group candidates, combined with a detailed ab-initio calculation of the formation and vibrational energy, have shown the structural model with space group P42/m (# 84) to be the best candidate combining the lowest energy and highest symmetry [5]. For the γ-phase, a structural candidate with orthorombic space group Pbca (# 61) has been found [5]. Ab-initio calculation has shown these models to be stable with similar energy compared to the the α-phase, explaining the coexistence of α-phase, γ-phase and β-phase in the range 20°C to 290°C.

References

HYDROGEN IN THE ATMOSPHERE

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Molecular hydrogen (H$_2$) is one of the most abundant trace gases in the atmosphere. It has recently become of wider atmospheric interest for various reasons among which is the ongoing discussion on switching our fossil-fuel based economy to a hydrogen-based economy. Such a potential change may result in drastic changes of the atmospheric H$_2$ budget. To better predict the impacts of enhanced anthropogenic H$_2$ usage to the atmospheric H$_2$ budget, better constraints on the currently poorly known budget are a prerequisite. For this reason attempts are being made to understand and quantify actual sources and sinks of H$_2$ to the atmosphere.

Introduction

H$_2$ is often regarded as a key component in the future energy chain. Consequently, several governments intensified their support of the development of hydrogen technology and infrastructure. Before the hydrogen economy becomes reality, the impact of the different emissions on the atmosphere should be investigated in detail and the current budget has to be entirely understood. We summarize the state-of-the-art knowledge of the H$_2$ budget and the current understanding of H$_2$-related processes in the atmosphere.

Results

We investigate H$_2$-related processes in the atmosphere by means of chassis dynamometer measurements, highway tunnel studies [1] as well as air quality monitoring at a suburban sampling site near Zurich [2] and at a high altitude research station (Jungfraujoch; 3580 m asl). The integration of all these measurements allows assessing the source of the automobile exhaust of H$_2$, evaluating the trend of anthropogenic H$_2$ emissions, assessing the H$_2$ uptake by soils as well as a determination of the current background atmospheric H$_2$ loading, trend analysis and an investigation of long-range transport of H$_2$.

Fig. 1 exemplarily shows the time series of H$_2$ accumulation (tunnel exit minus tunnel entrance) in a highway tunnel. It exhibits a strong diurnal cycle with highest concentrations during the morning and evening rush hours. This illustrates the dominant role of traffic emissions on the H$_2$ levels in the tunnel. On weekends, morning and evening peaks are less pronounced.

Fig. 1. Time series of H$_2$ accumulation in a highway tunnel.

References


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THE VIBRATIONAL SPECTROSCOPY OF HYDROGEN ADSORBED ON MICROPOROUS SYSTEMS.

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The most recent results concerning adsorption and storage of hydrogen on high surface area materials (zeolites, MOFs, polymers both pure and functionalized) are reviewed. It is shown that vibrational spectroscopy is a powerful tool to investigate the interaction forces governing the adsorption/desorption processes.

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DESTABILISED FLUORITE-STRUCTURED MG-BASED HYDROGEN STORAGE MATERIALS

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Introduction
It has been shown that alloying Mg with Sc enhances the kinetics of hydrogen insertion and extraction dramatically."". It was argued that the origin of these enhanced kinetics is related to the favorable crystallographic fluorite structure of the hydride.

Results
An interesting alternative for Sc was shown to be Ti which also forms a fluorite structure in its elemental hydride form. Interestingly, Ti does not form stable compounds with Mg under standard alloying conditions but it has recently been shown that meta-stable alloys can be prepared using non-equilibrium deposition methods."". These binary MgTi compounds combine a high hydrogen storage capacity"" (Fig. 1, curve (b)) with attractive optical properties."".

It will be shown by using in situ electrochemical XRD measurements that also in this case the favorable kinetics is related to the specific fluorite structure (Fig. 2). By adding a third element to these meta-stable MgTi compounds we recently succeeded, in accordance with the Miedema rule of reversed stability, to partially destabilize the hydrides to a much higher hydrogen pressure of ~0.1 bar at room temperature. Typical examples, such as MgTiAl shown in curve (a) of Fig. 1, will be discussed together with the simulation results of the corresponding isotherms."".

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References
SCALING UP EFFECTS OF Mg HYDRIDE AS A MATERIAL FOR HYDROGEN STORAGE

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A research program addressed to evaluate the magnesium hydride storage potentiality in stationary applications is being developed in the frame of a collaboration between CESI RICERCA, Milano, and the Hydrogen Group of Padova University. As a first step of scale-up effects evaluation, that are of major importance in industrial components, a storage system containing 500g of magnesium hydride powder (manufactured, using high energy ball milling, by Venezia Tecnologie SpA) has been designed and tested in different operating conditions in a fully automated test facility. The geometry design of the storage system has been carried out with the aim of ensuring a good heat exchange in order to overcome the low thermal conductivity of the hydride powder. A series of absorption and desorption cycles at different temperatures and pressures has been tested and the results have been compared with laboratory data obtained on small amounts (fraction of g) of powder samples. During the first cycles the behaviour of the scaled up system was rather similar to that of laboratory samples: maximum storage capacity of 5.35 wt% and hydrogen absorption and desorption kinetics slightly worse. Important thermal effects characterised by local powder heating has been noticed; a sensible performance degradation has been recorded after about 20 cycles, presumably due powder fragmentation and subsequent compaction that reduced the overall storage capacity of about 50%. Subsequent tests on a smaller storage system equipped also with porous baffles gave useful indication for the design of an improved large storage system.

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COMBINED PLATINUM / PEROVSKITE CATALYST FOR AN EFFICIENT NANOSTRUCTURED AIR ELECTRODE

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By combining platinum and the two perovskites La$_{0.6}$Sr$_{0.4}$CoO$_3$ (LSC) and La$_{0.65}$Sr$_{0.35}$MnO$_3$ (LSM) on a carbon nanotube (CNT) support air electrodes for fuel cells or zinc air batteries are produced, having fewer losses than a conventional Pt electrode. It is possible to reduce the amount of Pt up to 62 % compared to a conventional “Pt on carbon” electrode, which implies cost reductions up to 57 %. LSC has a positive impact on the activation polarization and LSM on the concentration polarization.

Introduction
In this work we demonstrate that a combined catalyst of LSC and LSM perovskites and Pt on a carbon nanotube support displays a smaller polarization in the whole current range than a conventional “Pt on carbon” electrode, although considerably less Pt is used.

Experimental
LSC and LSM perovskites, Pt on carbon, CNTs, PTFE dispersion and distilled water were mixed ultrasonically. After drying the resulting powder was sintered at 350 °C for 2 hours. Then the powder was mixed with petroleum to make a paste which was spread on teflonized Toray Carbon Paper, serving as gas diffusion layer. The two layers, catalytic active layer and gas diffusion layer, were pressed together and heated to 320 °C for 1 hour. A three electrode arrangement was chosen to measure the steady state current potential curves in alkaline solution.

Results
As shown in Fig. 1 the addition of Pt lowers the activation polarization at low current densities significantly compared with the electrode composed only of LSC and CNTs.

The addition of Pt is necessary to compete with conventional “Pt on carbon” electrodes. However, up to 62 % Pt can be saved and an electrode which is superior in the whole current region is obtained. The addition of small amounts of LSM (5 - 10 wt%) lowers the concentration polarization compared to the electrode consisting of LSC, CNTs and Pt.

Fig. 1. Steady state current potential curves of air electrodes with different compositions.

References
A Cu/Pt Near-Surface Alloy for Water-Gas Shift Catalysis Studied by STM, XPS, TPD, and DFT

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The water-gas shift (WGS) reaction, in which carbon monoxide (CO) and water (H₂O) react to form carbon dioxide (CO₂) and hydrogen (H₂), is an important step in the production of clean (CO free) hydrogen from fossil fuels. WGS catalysis is also an integral part of the onboard reforming of, e.g., methanol in low temperature fuel cell vehicles. For such mobile applications weight and volume is a critical issue, and it remains a challenge to design WGS catalysts with high activity at low temperature and thereby reduce the overall size of the reforming units.

In this study we use a combination of scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and density functional theory (DFT) to study a bimetallic Cu/Pt model catalyst for the WGS reaction [1]. From STM, XPS, and DFT we find that when Cu is evaporated onto Pt(111) at high temperature (800 K) a thermodynamically stable surface alloy is formed. The topmost atomic layer in this surface alloy consists purely of Pt, and the Cu atoms are embedded in the subsurface layers with the highest Cu concentration in the first subsurface layer. The TPD measurements show that the subsurface Cu atoms weaken the binding of CO to the topmost Pt layer, thus minimizing the risk of CO poisoning of the surface. This observation is confirmed by DFT calculations. Furthermore, the DFT calculations show that the Cu/Pt(111) surface alloy effectively activates water, while only binding the reaction products (CO) and reaction intermediates (formate) weakly. Water activation is the rate limiting step in WGS on several transition metals including Cu and Pt, and the DFT calculations therefore suggest that the bimetallic Cu/Pt catalyst is a promising candidate for an improved WGS catalyst.

References

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THIN-FILM ELECTROCATALYSTS FOR PEM FUEL CELLS

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Fundamental processes in PEM fuel cells are studied by use of well-characterized nanometer-thick catalyst films deposited on Nafion membranes or gas diffusion layers. The activity for oxygen reduction reaction, stability and proton conduction is evaluated for platinum in combination with a range of metals and metal-oxides in a single cell set-up. In addition, the samples are structurally and chemically characterized with TEM, SEM and XPS.

Introduction

The catalyst material in the PEM fuel cell needs to be improved with respect to performance and durability. Well defined nanostructures are convenient model systems to study governing mechanisms. Recently, we have developed a route to manufacture model systems in a fast and relatively easy manner, with high control over structure and composition. The samples are possible to evaluate under realistic fuel cell operating conditions in a real fuel cell.

Experimental

Nanometer thick catalyst films (~5-10 µg/cm\textsuperscript{2}) have been deposited on to Nafion membranes and gas diffusion layers by thermal evaporation in vacuum. A large range of catalyst materials have been tested including Pt mixed with Au, Ir and TiO\textsubscript{2}. The morphology and composition of the thin films are thoroughly characterized with TEM, SEM and XPS.

Results

The thin-film model system can be used to qualitative compare and rank catalyst material in the PEMFC environment. Clear changes in the catalytic and structural properties of Pt were observed when the metal was mixed in bi-layers with Ir and TiO\textsubscript{2}. TiO\textsubscript{2} was found to operate as a proton conducting electrolyte in the PEMFC.

In addition, adding TiO\textsubscript{2} between Pt and the carbon gas diffusion layer indicated an increased durability of the PEMFC electrode.

References


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HIGH-THROUUTHPUT AND COMBINATORIAL METHODS USED FOR HYDROGEN TECHNOLOGIES. DESIGN OF CATALYSTS FOR PRODUCTION AND PURIFICATION OF HYDROGEN.

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Different catalyst libraries were designed and tested for hydrogen production via ethanol reforming and for CO removal from hydrogen containing gas mixture (PROX). Multi-component gold based supported catalysts over MgO and Al₂O₃ were designed for PROX application. In ethanol reforming Pd, Ni, and Co based catalysts were tested. In PROX modification of the support by Pb, Sm, Ba, Ce and V resulted in very active and selective catalysts. The optimum composition of catalysts strongly depended on the type of support and the mode of pre-treatment prior to the reaction.

Introduction

Hydrogen technologies require new materials, such as catalysts, adsorbents, membranes etc. The use of high-throughput and combinatorial methods (HTCM) strongly increases the change to find these materials. In this work results obtained in various case studies related to design of new catalysts will be given.

Experimental

The high-throughput reactor setup applied is described elsewhere [1]. HRS and its combination with ANNs as an information mining tool [2] was used for catalysts design. Urea method was applied for the preparation of multi-component supports and the introduction of gold. Reduction in hydrogen at 350 °C was used as a general pretreatment procedure, what was also combined by more complex pretreatment procedures.

Results

In PROX two methods for catalysts pre-treatment were compared. After reductive treatment the optimum catalyst contained Au, Pb, Sm, Ce, Y and La, while after combined reductive treatment the Au required only Pb and Sm and V as modifiers. The visualization of these experimental spaces is given in Fig 1.

![Fig. 1. Visualization of the experimental space in PROX reaction over modified Au/MgO catalysts](image)

The alumina support required completely different modifiers, such as Pb, Cu, Ba, Ag etc. Results unambiguously show the advantage of HTCM in catalyst development for hydrogen technologies.

References


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PHOTOCATALYTIC WATER DISSOCIATION AT GRAPHITE/ICE INTERFACE

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We have studied the photodissociation of water molecules at the ice/graphite interface in the presence of submonolayer amounts of potassium at UHV conditions. The ice films are transparent for 240 – 900 nm photons, but the strong light absorption of graphite substrate generates energetic charge carriers that may drive photoreactions at the interface. Similar schemes have been demonstrated and investigated before in the monolayer regime¹. Here, using ice films of tens of monolayer thickness and with different structure, we investigate the confinement effects due to the ice layer, and the ice permeability for reaction products.

Introduction

Significant fraction of visible light has enough energy to split H₂O into hydrogen and oxygen. However, water is transparent in the visible and does not absorb this energy. The combination of a light harvesting system and a H₂O splitting system is thus necessary. We are exploring a graphite substrate, covered with small amounts of alkali atoms, because it is an interesting model system for photoreactions at surfaces and in particular H₂ production.

Experimental

The experiments were performed at ultra high vacuum conditions in the low 10⁻¹⁰ mbar range. The ice films were grown on the basal plane of highly oriented pyrolytic graphite at LN₂ temperatures. Irradiation was performed in either pulsed or continuous (cw) regime using Nd:YAG laser pumped OPO (Continuum) system, or short arc lamp system (PI). For detection and direct monitoring of the photodesorbing products we used quadrupole mass spectrometers.

Results

H₂, CO and CO₂ were seen as main desorbing photoreaction products immediately upon irradiation. The proposed mechanism is schematically illustrated on Fig. 1. Central for this study² was to elucidate the role of ice structure on reaction outcome. While CO and CO₂ were trapped by (poly)crystalline ice, H₂ is able to permeate through both amorphous and annealed films. CO and CO₂ were still generated under the ice cover during the irradiation and released later when the ice (re)crystallizes or sublimates. Some of the reaction products could be trapped inside the ice.

References


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HY.MUVE – HYDROGEN DRIVEN MUNICIPAL VEHICLE

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Municipal vehicles (road sweepers) are an ideal platform for the early introduction of fuel cell power trains for various technical and non-technical reasons, among them: for most of the time (in cleaning mode) these vehicles run at low loads, where fuel cells are highly efficient. As operation is local, a small hydrogen infrastructure is sufficient, “zero emissions” allow use in closed areas as shopping malls or train stations and as operation takes place in public, high visibility and publicity is possible. In the Hy.muve project a road sweeper will be equipped with a fuel-cell-hybrid drive train and run in practice for 18 months. This allows gaining knowledge in complex drive train layout, practical realisation questions, real world ageing of fuel cells and socio-economic aspects of development, production, usage and public awareness.

Project goals
- 50% energy consumption reduction compared to existing diesel vehicle. I.e. less than 7.5 kg of hydrogen used for one 8 hour shift.
- Pre series demonstrator running 18 months in practice in 3 cities.
- Socio-economic research regarding new production channels, market preparation and introduction of H₂ powertrains.

Drivetrain layout and optimisation
The originally hydraulic drive trains of traction chain and vacuum-ventilator are electrified for better efficiency
The fuel cell is hybridized with a battery for recuperating energy while breaking or driving downhill.

Efficiency optimisation
To optimise the drive train components to an overall best efficiency, a characteristic load cycle for a one day shift was developed by assistance of operators in different cities of Switzerland. This test cycle contains a speed diagram, a slope distribution and a realistically growing load of the vehicle. In the speed diagram three dislocation phases of 30 min and 6.5 hour of cleaning are assumed.

By optimising fuel cell and battery size, a fuel consumption of less than 5 kg of hydrogen was achieved.

Well to wheel estimation
As in this application the fuel cell runs near its best point for long phases, a well to wheel analysis even assuming the today’s non optimal H₂ production out of natural gas shows that this fuel cell approach is superior to CNG-electric or diesel electric drive trains.

![Fig. 1. Comparison of well to wheel energy consumption and CO₂ production.](image)

References

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THERMAL PROPERTIES OF Mg(BH₄)₂ DOPED WITH TRANSITION METAL CHLORIDES

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Hydrogen storage materials based on complex hydrides, such as tetrahydroaluminates, tetrahydroborates, and amides, have been considered promising for reversible hydrogen storage. [1-3] Materials consisting of light elements have also drawn attention due to the high gravimetric storage capacities for hydrogen and especially, Mg(BH₄)₂ seems to meet the requirements for hydrogen storage material because it contains 14.9 mass % and has suitable thermodynamics properties. [4, 5]

The main disadvantages of Mg(BH₄)₂ as hydrogen store is the high absorption/desorption kinetic barriers. Transition metal compounds such as MCl₃ (with M = V, Ti, Mo, Ce) were added to Mg(BH₄)₂ in order to lower these kinetics barriers. X-ray diffraction measurements (XRD) and thermogravimetric analysis (TGA-DSC) of the samples after mechanical ball-milling will be presented.

References


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IMPROVING RHC COMPOUNDS PREPARATION BY BALL MILLING

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The NaBH₄ is one of the light-complex hydrides most studied in the field of hydrogen storage. It has a high theoretical hydrogen capacity of 10.8 wt% and it is relatively cheap. But, its decomposition temperature is close to 400°C and the destabilization of NaBH₄ by ball milling is also very difficult because it is quite resistant to formation of nanostructure. Nevertheless, the destabilization of this compound can be obtained by the addition of reactive hydrides, such as MgH₂. This approach can be utilized also for others complex hydrides. It generates a new class of compounds called “Reactive Hydride Composites”, which are obtaining a great interest as a new potential hydrogen storage material.

This work presents a systematic study of the RHC basis NaBH₄ preparation by two different milling machines. In order to provide a basis of comparison for the milling process with either Spex 8000 or Fritsch Planetary milling device, the powders of NaBH₄ + MgH₂ have been mixed in a ratio of 2:1 under Ar for 5 hours with the ball-to-powder (BPR) weight ratio of 10:1. A further preparation has been carried out in the same milling conditions, except for the addition of an additive. Thermal and structural properties have been investigated by Differential Scanning Calorimetry (DSC) and X-ray Diffraction (XRD), respectively. Microstructure has been studied using Scanning Electron Microscopy (SEM). The hydrogen desorption after milling has been monitored by Integrate Microbalance System (IMS) integrated with a mass-spectroscopy.

With the purpose to optimize the preparation methods for the RHC samples, the correlation between the particles and crystallites size and the desorption temperature is discussed. A comprehensive structural study at different temperatures regarding the sample milled with an additive is here presented.
MICROSTRUCTURAL AND CHEMICAL STUDY OF 2LiBH₄+MgH₂ REACTIVE HYDRIDE COMPOSITE FOR H₂ STORAGE

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Hydride composite systems reveal great potential as hydrogen storage materials as they overcome the thermodynamic limitations hindering the use of light-weight complex hydrides. In the present communication the effect of Ti-based additive has been studied in the system 2LiBH₄ + MgH₂. The microstructure is characterized by X-Ray Diffraction (XRD) and Transmission Electron Microscope (TEM) in the milled and cycled states.

X-Ray diffraction in transmission mode has been used to identify the crystalline phase present in the samples. Moreover, the microstrain and the crystallite size of the different phases were calculated by the Williamson-Hall method.

The materials were observed by Transmission Electron Microscope for microstructure analysis. Energy Dispersive X-Ray Analysis (EDX) was used to determine the elements present in the samples and Electron Energy Loss Spectroscopy (EELS) to register the energy loss spectra of Boron, Oxygen and Titanium and determine the location of the Titanium based additive in the sample.

For both samples after milling, the LiBH₄ showed larger crystal size than MgH₂. Besides, the microstrain is found to be one order of magnitude larger for both phases milled with the additive. After desorption, this sample evolves to a mixture of LiH and MgB₂ phases with reduced levels of microstrain. The crystal sizes of both phases are found to be similar, and intermediate between the ones of the preceding LiBH₄ and MgH₂ phases. The crystal sizes of the desorbed products in presence of additive are smaller than the ones of the desorbed from 2LiBH₄+MgH₂ milled without additive.

The first results from TEM investigations coupled with EDX and EELS show in the composite materials 2LiBH₄ + MgH₂ two regions: one mainly consisting of Mg and a second one which appears to be amorphous and is containing a high amount of Boron.

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IN-SITU MONITORING DURING SYNTHESIS OF LiBH₄ AND Mg(BH₄)₂ BY BALL MILLING UNDER DIFFERENT PRESSURES AND ATMOSPHERES

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The synthesis of LiBH₄ and Mg(BH₄)₂ by ball milling under different pressures and atmospheres was monitored by means of dedicated milling vials. This allowed the tuning of parameters such as ball-to-powder ratio, initial pressure, milling duration and catalyst addition. The synthesis of LiBH₄/MgH₂ composites from a mixture 2LiH + MgB₂ was expected to occur under high-pressure reactive milling, whereas the synthesis of Mg(BH₄)₂ from a mixture 2LiBH₄ + MgCl₂ was expected to occur already under 1 bar Ar. The efficiency of TiCl₃ and Ti-isopropoxide as catalysts for these reactions was studied. X-ray powder diffraction and Raman spectroscopy of the as-milled powders were carried out to confirm the data obtained during synthesis.

Introduction
Borohydrides have recently received increasing attention as potential materials for on-board hydrogen storage. The aim of the present work is the formation of LiBH₄/MgH₂ composites and Mg(BH₄)₂ by ball milling under different pressures and atmospheres.

Experimental
Starting mixtures of 2LiH + MgB₂ and 2LiBH₄ + MgCl₂, with and without catalyst, were milled together with stainless steel balls (10 mm Ø) at different ratios. The initial milling pressure was chosen between 1 bar Ar, and 1 and 135 bar H₂ at room temperature. The milling duration was varied from 5 to 20 h. The reactions occurring during milling were monitored by means of specially designed vials (by Evico Magnetics). Pressure (p) and temperature (T) variations were recorded [1]. The as-milled powders were characterised by X-ray powder diffraction (XRD) and Raman spectroscopy.

Results
In the case of 2LiH + MgB₂, the results showed almost constant p and T curves for the samples milled with no catalyst or with Ti-isopropoxide under initial pressures of 50 bar H₂. This indicated that no reaction was taking place between the compounds and the surrounding H₂ under these conditions. In contrast, the samples milled with TiCl₃ showed a distinctive pressure decrease occurring after 2.5 h of milling. The decrease was found to be stronger in the case of the sample milled under 135 bar H₂. The diffraction pattern of the resulting powder showed no traces of LiBH₄ or MgH₂, but the presence of small amounts of LiCl, and the absence of strong LiH traces, indicated that at least a portion of the TiCl₃ reacted with LiH during the process. On the other hand, the ball milling of 2LiBH₄ + MgCl₂ mixtures under 1 bar Ar, showed no identifiable features on the monitored curves. In the case of a sample milled for 12 h, the XRD traces of LiBH₄ and MgCl₂ were found to disappear whereas a Li-Mg-Cl phase with the structure of LiCl was identified. Although no traces of Mg(BH₄)₂ were identified by XRD, Raman spectroscopy confirmed the partial formation of magnesium borohydride consistent with the results by Nakamori et al. [2] and Matsunaga et al. [3].

References

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Li[BH₄] AND Li[BD₄] SYNTHESIS FROM Li-B ALLOY

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The direct synthesis of Li[BD₄] and Li[BH₄] from the corresponding elements is demonstrated. For the Li[BD₄] the formation was achieved at T = 350°C and p(D₂) = 180 bar. The chemical inertness of boron is thought to prevent its reaction with lithium and deuterium/hydrogen to Li[BD₄]/Li[BH₄] at lower temperatures. We show however that the reaction kinetics can be enforced by a LiB₃ like alloy which is formed in inert argon atmosphere at 330°C. The synthesis of the boranate is carried out by exposing the Li-B alloy to a defined deuterium/hydrogen pressure in a high pressure stainless steel vessel and the adsorption is monitored by the pressure decrease in the system (for the Li[BH₄]) or by “in situ” neutron powder diffraction (for the Li[BD₄]).

Introduction
In this work an improved direct synthesis of Li[BD₄]/Li[BH₄] from the elements is presented based on a preceding formation of a LiB₃ alloy [1-2]. An analysis of the absorption reaction is performed in order to describe the mechanism. Thereby “in situ” neutron diffraction is applied to study the absorption process.

Experimental
The starting material for the synthesis is a mixture of Li and pre-milled B of stoichiometric ratio 1:3. Heating the Li/B mixture for 60 h at 330°C in Ar atmosphere leads to the formation of a LiB₃ alloy [3]. The sample was then heated in deuterium/hydrogen from room temperature (RT) to 700°C (for H₂) or from RT to 500°C (for D₂) in a high pressure stainless steel cylinder. For the hydrogen sample the hydrogen uptake was monitored by the pressure changes in the system and for the deuterium sample neutron diffraction patterns were taken for different temperatures.

Results
We demonstrated the preparation of solvent free Li[BD₄] and [Li[BH₄]] from the elements. For the Li[BD₄] the synthesis was achieved at a deuterium pressure of 180 bar and a temperature of 350°C. This improvement is accomplished by a pre-formation of a LiB₃ alloy heating Li and pre-milled boron in inert gas atmosphere. The hydrogen uptake and neutron diffraction measurements during heating of the LiB₃ alloy in H₂/D₂ reveal different reactions of boranate formation taking place (see Fig. 1). These reactions are temperature dependent.

References
[2] Remhof et al., to be published

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The mass flow measurement can be used for the thermodynamic characterization, $\Delta H$ and $\Delta S$, of hydrogen storage materials by determining equilibrium pressures at zero-flow. Moreover, flow measurements provide information about reaction kinetics. In this work, hydrogen desorption kinetics by LaNi$_5$ was measured at 293 K. The result indicates that the mass flow method is of great use in kinetic characterization and to explore future hydrogen storage materials.

**Introduction**

With a conventional volumetric method, i.e., Sieverts’ type apparatus, a slow reaction rate causes significant difficulty in the determination of p-c-isotherms and thermodynamic properties due to a long reaction time and the incidental system errors. A MF (Mass flow) measurement which gives dynamic p-c-isotherms is advantageous to a slow-kinetic material and can be applied to the thermodynamic characterization, namely, for van’t Hoff plot with equilibrium pressures extrapolated to zero flow rate [1, 2]. On the principle, a MF-method gives kinetic information and can also be utilized for reaction kinetic study. In this work, desorption measurement of LaNi$_5$ was demonstrated.

**Experimental**

The sample was activated by 16 hydriding-dehydriding cycles prior to the subsequent measurements. A Mass flow controller was used to calculate the amount of hydrogen evacuated during a desorption measurement. BET surface area was measured after a series of the measurements. Reaction probability (i.e. recombination probability for desorption process), which is defined as the ratio of the reaction rate to the impinging rate of hydrogen molecules, was used for the assessment of the reactivity of hydrogen molecules on the sample surface [3].

**Results**

Desorption measurement of LaNi$_5$ revealed that the MF-method is of great use in the kinetic study, especially, focusing on a plateau region of the p-c-isotherm. This work exhibits potential to access information about the surface properties of hydrogen storage materials.

**References**


THERMOGRAVIMETRY OF Li[BH₄]

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The magnetic suspension balance allows the thermogravimetry measurements of hydrides. The control of temperature, pressure and mass takes place simultaneously and with high accuracy. As a first example it presents the thermogravimetry of LiBH₄.

Introduction

The magnetic suspension balance is able to determine the equilibrium pressure by measuring the mass with high accuracy under controlled conditions of temperature and pressure. From this it is possible to calculate the heat of formation. The thermodynamic and kinetic aspects can be studied.

Setup

In the suspension balance the sample is not hanged directly at the balance but it links to a "suspension magnet". This consists of a permanent magnet, a sensor core and a device for decoupling the measuring load and it is freely suspended state maintained by an electromagnet controlled via electronic unit. Sample handing takes place in an Ar-glove box. The microbalance is located outside the argon box and measures the force transmitted by magnetic suspension coupling inside the measuring chamber.

Fig. 1 Magnetic Suspension Balance

Kinetics

The kinetics can be studied by measuring the mass of the sample at constant temperature and pressure changing or at constant pressure and varying the temperature (so-called thermodesorption spectroscopy)

Fig. 2 Thermodesorption of LiBH₄ in bar hydrogen. Heating rate is 1 K/min.

The Fig. 2 shows the thermodesorption spectra of LiBH₄ in 1 bar of hydrogen. From the mass change (bottom panel) the desorption rate (top panel) is derived. Significant rates are observed at melting point (268 °C) and the desorption process is completed in the second step at 400°C.

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STABILITY OF Na[BH₄]

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The stability of NaBH₄ was investigated by pCT- (pressure, concentration, Temperature) measurements under constant hydrogen flows and extrapolated to equilibrium. From Van 't Hoff equation the following thermodynamic parameters are derived for desorption: enthalpy of reaction \( \Delta H = 108 \text{ kJ mol}^{-1} \text{H}_2 \) and entropy of reaction \( \Delta S = 133 \text{ J K}^{-1} \text{mol}^{-1} \text{H}_2 \). NaBH₄ decomposes to NaH + B + 3/2 H₂ and can theoretically release 10.7 wt% of hydrogen for this reaction.

Introduction

In this work the enthalpy \( \Delta H \) and entropy \( \Delta S \) of reaction of the desorption of NaBH₄ were determined by pCT-measurements. The logarithm of the equilibrium pressure \( p_{eq} \) divided by standard pressure \( p_0 = 1.01325 \text{ bar} \) as a function of the inverse temperature is represented in a Van 't Hoff plot and \( \Delta H \) and \( \Delta S \) are determined according to the Van 't Hoff equation:

\[
\ln \left( \frac{p_{eq}}{p_0} \right) = \frac{\Delta H}{R} \cdot \frac{1}{T} - \frac{\Delta S}{R}
\]

The slope of the straight line is proportional to \( \Delta H \) the axis intercept is proportional to \( \Delta S \).

Experimental

For the pCT measurements 250 mg of NaBH₄ from Sigma-Aldrich were heated to temperatures between 600°C and 700°C under a pressure of 1 bar hydrogen. The measurements were performed at different constant hydrogen flows of 0.5, 1 and 2 nccm respectively.

Results

The different plateau pressures for the different temperatures and flows are shown in Fig. 1. Because the plateau pressures depend on the applied flow \( \ln(p_{eq}/p_0) \) as a function of the flow is extrapolated to the equilibrium (0 nccm) (black squares) [1]. From the Van 't Hoff equation the following values were found: enthalpy of reaction \( \Delta H = 108 \text{ kJ mol}^{-1} \text{H}_2 \) and entropy of reaction \( \Delta S = 133 \text{ J K}^{-1} \text{mol}^{-1} \text{H}_2 \). The decomposition temperature as derived from the presented pCT measurements \( T = 536°C \) is in good agreement with that derived from thermodesorption \( T = 565°C \) (from [2], [3]).

Fig. 1. Van 't Hoff plot of NaBH₄ (desorption).

References

[3] S. Orimo, Y. Nakamori, A. Züttel, Material Properties of LiBH₄ (M=Li, Na and K), Materials Science and Engineering, 2004

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The “Science of Hydrogen & Energy” award is a prize, just similar to the Nobel price, for an extraordinary contribution to the sciences of hydrogen. The aim is to award a prize to a distinct scientist for his scientific work of a life time.

Louis Schlappbach started his scientific work in 1970, 38 years ago, with the investigation of the Hall effect, electrical transport and magnetic susceptibility of liquid rare earth elements like Cerium. 30 years ago in 1970 he was coauthor with Busch and Waldrich on a paper about the hydrides of La-Ni compounds. LaNi5 was subsequently investigated in view of the structure, surface segregations, hydrogen occupation of interstitial sites and as electrode material. LaNi5 is still the base material for most of the electrochemical applications of metal hydrides today. The work on LaNi5 was complemented by the research on FeTi. Louis Schlappbach realized the importance of the surface composition for the hydrogen sorption process and he was able to describe the role of the surface-active species. Furthermore, he investigated the changes of the surface composition of LaNi5 and FeTi in oxidizing atmospheres and he found the formation of metallic clusters as superparamagnetic particles acting as the active sites in hydrogen dissociation and recombination. The investigation of the surface of metal hydrides was further intensified by means of X-ray photoelectron spectroscopy. Louis Schlappbach was the first scientist correctly describing the activation process of a metal hydride and, furthermore, to model the chemical composition and states of the elements in a surface profile. He also succeeded to analyze the electronic structure of rare earth elements and their hydrides by means of photoemission spectroscopy.

In 1990 Louis Schlappbach edited the two books “Hydrogen in Intermetallic Compounds I & II” of the Springer Series. The books became a very important reference for all the researchers active in the field of hydrides.

Louis Schlappbach’s work is highly appreciated in the worldwide hydrogen community and his contribution to the scientific knowledge is of an enormous importance. Numerous undergraduate students, PhD students and Post Docs have been educated by Louis in solid state physics and the sciences of hydrides. Therefore, we are very proud to award Louis Schlappbach with the second Science of Hydrogen & Energy prize.
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INFORMATION
Braunwald is car-free and only reachable by train (funicular railway). The latest departure time in Zürich airport is 20:47 to reach Braunwald on the same day. Please use the following website for train connections:

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