The 5th symposium “Hydrogen & Energy” follows the 4th symposium on 24. – 29. January 2010 in Wildhaus with more than 80 participants. It serves as an information platform of the fundamental science and technology and the frontiers of research on hydrogen and energy.

The symposium consists of invited keynote lectures reviewing the key elements of the hydrogen cycle, i.e. the hydrogen production, hydrogen storage and hydrogen combustion and fuel cells. Furthermore, contributions on the conversion of renewable energy in general and energy carriers beside and beyond hydrogen are very welcome. The world leading experts present the current research challenges and most important results in invited and contributing talks. Early stage and experienced researchers present their newest results and the open questions on posters as well as in a one slide presentation.

The conference will take place in the conference and wellness hotel Stoos in the beautiful small village Stoos on 1'270 m above sea level. The village is free of traffic on a alp above Schwyz in central Switzerland.

The number of participants is limited to 80.


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SCIENCE OF HYDROGEN & ENERGY AWARD

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Abstracts
HYDROGEN ENERGY: Policy responses to economic and social challenges

Paul Ekins
UCL Energy Institute, University College London, Central House, 14 Upper Woburn Place, London WC1H 0NN, UK

Hydrogen as an energy vector has been subject to waves of enthusiasm as to its potential to resolve pressing concerns of climate change, energy security and local pollution resulting from the use of other fuels. Sometimes this has obscured the very real technical, economic and social challenges that need to be successfully addressed if this potential is to be realised in practice.

Hydrogen Technologies and Applications

A range of more or less complex technologies is involved in the production, storage and distribution of hydrogen, and it may be may put to a variety of end uses in vehicles, as auxiliary power units or for stationary power provision.

Hydrogen Economics and Policies, and Social Implications

Very considerable technical innovation will be required for hydrogen to break out from current niche applications into the mass markets that could bring about its widespread use [1]. The innovation will need to improve its performance economically and technically, with a technological diffusion process likely to take place over decades through a transition that transformed the current energy infrastructure and end-use applications [2]. Hydrogen is emerging in different places in different ways, in each case as a result of public policies, devised to achieve specific local and regional economic or environmental objectives.

Current levels of public knowledge about hydrogen are very low, and systematic public engagement is required to ensure that the technologies win acceptance. The policies required to bring about the widespread diffusion of hydrogen will need to range from basic R&D through to demonstration projects and public support for infrastructure provision and diffusion of the key applications.

References


Paul Ekins

Born 24. 7. 1950 in Djakarta, Indonesia, before family moved back to UK. 1971 Electrical Engineering Degree from Imperial College London. 1988 Masters in Economics from Birkbeck College London 1996 PhD in Economics from Birkbeck College London 1996-2002 Senior Lecturer then Reader then Professor of Sustainable Development, Keele University 2002-07 Head, Environment Group, Policy Studies Institute and Professor of Sustainable Development, University of Westminster. 2002-08 Member of the UK Royal Commission on Environmental Pollution 2008-09 Professor of Energy and Environment Policy, King’s College London 2009-now Professor of Energy and Environment Policy, UCL Energy Institute, University College London. Books include Economic Growth and Environmental Sustainability: the Prospects for Green Growth (Routledge, 2000). 1994 Global 500 Award ‘for outstanding environmental achievement’ from United Nations Environment Programme

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Impact of Nanoconfinement and Additives on the Hydrogen Sorption in Boron Hydrides

Peter Ngene, Roy van den Berg, Petra de Jongh
Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands

Boron hydrides have a high hydrogen content, and hence are interesting hydrogen storage materials. However, generally the kinetics for hydrogen desorption are sluggish, and (partial) reversibility can only be achieved at high temperatures. Confining the phases on a nanoscale, especially combined with certain additives, has a large impact on the hydrogen desorption kinetics and reversibility.

Nanoconfined boron hydrides
Complex metal hydrides were loaded into mesoporous carbon scaffolds by techniques such as melt infiltration and pore volume impregnation. N\textsubscript{2} physisorption allowed assessment of the pore filling. As the nanoconfined hydrides typically lacked long-range crystallinity, analysis of the phase evolution during cycling was based on solid state NMR, EXAFS, EM, and HP-DSC. In this contribution we discuss especially nanoconfined LiBH\textsubscript{4} and NaBH\textsubscript{4}.

Hydrogen sorption - reversibility
Not only hydrogen sorption kinetics are changed by nanoconfinement, but also thermodynamical stability and decomposition pathway. Another important aspect is reversibility, as illustrated in the Figure showing the H\textsubscript{2} uptake for LiBH\textsubscript{4}/carbon at 320 °C, 40 bar H\textsubscript{2}. Clearly nanoconfinement improves the reversibility under mild conditions\textsuperscript{1}. However, a small amount of additives leads to a significant additional enhancement of reversibility.\textsuperscript{2} These results will be related to the microstructural development during cycling.

References

Petra de Jongh received her PhD in photoelectrochemistry in 1999, and worked 5 years as a senior scientist at Philips Research. She is now associate professor at Utrecht University, where she (co)-supervises researchers working on supported nanoparticles, especially for applications in catalysis and energy storage and conversion.

P.E. de Jongh

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Hydrogen Storage in Nanoscale Binary Hydrides

Wiebke Lohstroh, Marcus Fehse, Arne Roth, Maximilian Fichtner
Institute of Nanotechnology, Karlsruhe Institute of Technology, P.O. Box 3640, 76021 Karlsruhe, Germany

Hydrogen storage properties of composites comprised of LiH, NaH and a carbon host material were investigated. Compared to the pure alkali metal hydrides, decomposition temperatures are lowered in all cases and reversible hydrogen uptake was obtained around 300°C. NaH containing samples showed only minor differences with porosity of the carbon host while different decomposition temperatures were found for LiH combined with graphite and activated carbon fibre, respectively.

Introduction
The binary hydrides LiH, NaH have a high hydrogen capacity (12.6 and 4.2 wt%, respectively) but they have also high thermodynamic stability. The release temperature for hydrogen is lowered when the materials are embedded in a carbon matrix [1,2]. Similar composites with NaAlH₄ or MgH₂ exhibit also changes of the thermodynamic properties [3,4].

LiH and NaH composites
Composites of NaH and LiH with carbon (graphite and activated carbon fibre) have been investigated for the hydrogen storage properties. All samples showed a lowered hydrogen release temperature compared to the pure alkali metal hydrides. At 300°C, the reversible hydrogen capacity is 0.2 H atoms per alkali metal atom. Likewise, LiH/NaH (with a molar ratio 1:1) mixtures with carbon can be reversibly cycled at 300°C with similar hydrogen contents. For Li-C samples the hydrogen release temperatures are shifted to higher temperatures and the formation of Li₂C₂ is favoured. For NaH containing samples the porosity of the carbon appears to be of minor importance while different decomposition temperatures were found for LiH combined either with graphite or activated carbon fibre.

References

Born 13. 04. 1972 in Bad Nauheim, Germany. 1996 Diploma in Physics, Georg-August Universität Göttingen, Germany 1999 Dr. rer. nat. from the science faculty Georg-August Universität Göttingen, Germany 2000 Post doc at the Clarendon Laboratory, Condensed Matter Physics, Oxford University 2003 Post Doc at the Department of Physics and Astronomy, Condensed Matter Physics at the Vrije Universiteit Amsterdam, The Netherlands 2005 Research Staff at the Institute of Nanotechnology, Karlsruhe Institute of Technology (then Karlsruhe Research Centre GmbH)

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Iodine Stabilized HT Phase of LiBH$_4$

Pascal Martelli$^{1,2}$, Arndt Remhof$^1$, Ralf Ackermann$^3$, Jan Peter Embs$^{3,4}$, Andreas Züttel$^{1,2}$

$^1$ Empa Swiss Federal Laboratories for Materials Science and Technology, Hydrogen & Energy, 8600 Dübendorf, Switzerland, $^2$ Physics Department, University of Fribourg, 1700 Fribourg, Switzerland, $^3$ Laboratory for Neutron Scattering, Paul Scherrer Institut, 5232 Villigen, Switzerland, $^4$ Saarland University, Physical Chemistry, 66041 Saarbruecken, Germany

LiBH$_4$ is known to be a reliable candidate for hydrogen storage material but recently it has shown another interesting property: it is a super ionic conductor at elevated T (>110°C). Mixed with LiI it shows a high temperature (HT) phase behaviour at low temperature. Quasielastic neutron scattering measurement (QENS) is used in order to observe the rotational motion of the BH$_4^-$ and therefore to confirm the HT phase stabilization.

**Experimental**

The measurements were carried out using the time-of-flight neutron spectrometer FOCUS located at the continuous spallation source SINQ at the Paul Scherrer Institute in Villigen, Switzerland.

Stabilization of the HT phase

Maekawa et al. [1] have discovered that adding some halides (Cl, Br and I) permit to stabilize the HT phase at LT even at RT. In order to better understand the diffusion process of the mixture LiBH$_4$-LiI, a systematic investigation has been made with QENS for several ratios (xLiBH$_4$-LiI, x=1,2,4). The dwell times of the rotations (ps range) vary with temperature (150-330K) and are fitted to the Arrhenius equation. Jumps length and frequency occurring inside the mixture has been determined as well as the activation energy and a confirmation of the stability of the HT phase below the RT.

**References**


Pascal Martelli  

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Building blocks of the system LiBH$_4$-LiNH$_2$-LiI

Andreas Borgschulte,$^1$ Andreas Züttel,$^1$ Motoaki Matsuo,$^2$ Shin-Ichi Orimo,$^2$

$^1$Empa Lab. Hydrogen & Energy, CH-8600 Dübendorf, Switzerland
$^2$Institute for Materials Research, Tohoku University, Katahira 2-1-1, Sendai, 980-8577, Japan

The pseudo-ternary phase diagram LiBH$_4$-LiNH$_2$-LiI is investigated. The various phases may be formed via the exchange of the neutral species NH$_3$ competing with the exchange of ions. Depending on the preparation method, NH$_3$ may be included as an additional building block.

The phase diagram LiBH$_4$-LiNH$_2$-LiI

The pseudo-ternary phase diagram LiBH$_4$-LiNH$_2$-LiI as sketched in the figure is a concept to summarize and predict compounds built from the three starting compounds.

However, this implies the existence and stability of the building blocks (pseudo-anions) BH$_4^-$ and NH$_2^-$. Upon mixing of LiBH$_4$-LiNH$_2$, the pseudo-ions are exchanged and form mixed compounds such as Li$_4$(BH$_4$)(NH$_2$)$_3$ [1] and solid solutions Li(BH$_4$)$_{1-x}$I$_x$,[2] with ionic compounds such as LiI$^-$. However, the borohydrides as well as imides are known for releasing neutral species, i.e. BH$_4^-$ respectively NH$_3$. Ammonia, in turn, forms stable compounds with LiI [3] and LiBH$_4$ [4]. The latter reactions proceeding via the exchange of a neutral species compete with the exchange of ions. Depending on the preparation method, NH$_3$ may be included as an additional building block.

Experiment

The existence and stability of the various phases are investigated via gradient samples probed by Raman spectroscopy and gravimetric thermo-desorption in combination with infrared gas analysis.

References


A. Borgschulte


Corresponding author: Andreas Borgschulte: andreas.borgschulte@empa.ch, Tel. (+41) (44) 823 4639
Improved Hydrogen Storage Properties of LiBH$_4$ by addition of Nickel

Yigang Yan, Hai-Wen Li, Masaharu Menjo, Shin-ichi Orimo
Tohoku University, Institute for Material Research, Hydrogen Functional Materials Division, Sendai 980-8577, Japan

LiBH$_4$ starts to decompose over the melting point, and release 13.8 wt% of hydrogen according to LiBH$_4$ $\rightarrow$ LiH + B + 3/2H$_2$ [1]. To reduce the dehydriding temperature of LiBH$_4$, an effective approach is to tailor the enthalpy change in dehydriding reaction by combination with metal or metal hydrides [2, 3]. By addition of nanosized nickle, the dehydriding and rehydriding properties of LiBH$_4$ were both significantly improved.

**Combined LiBH$_4$ system**

The combined systems such as LiBH$_4$-MgH$_2$, etc., show reduced enthalpy changes in dehydriding reaction and improved reversible hydrogen storage properties, due to the formation of metal borides (e.g. MgB$_2$, etc.) rather than elemental boron as the dehydriding product.

**Adjustment of Reaction Pathway**

The mixture of LiBH$_4$ and 25 wt% Ni was mechanically milled for 5 h. The hydrogen amount is referred to pure LiBH$_4$. Approximately 12.5 wt% of H$_2$ was released in LiBH$_4$ with and without Ni addition. The dehydriding temperature was reduced by approximately 90 K by addition of Ni. The equilibrium pressure ($P_{eq}$) of dehydriding reaction increases from 0.35 to 1.2 MPa, resulting in the reduction of enthalpy changes ($\Delta H$) from 76 to 68 kJ/mol H$_2$. The reduced $\Delta H$ suggests the thermodynamic improvement effect of Ni addition on the dehydriding reaction of LiBH$_4$, according to the reaction of LiBH$_4$ + 4/3Ni $\rightarrow$ LiH + 1/3Ni$_3$B$_3$ + 3/2H$_2$. The rehydriding amount of LiBH$_4$ at 823 K and 35 MPa H$_2$ is increased from 4.3 to 10.8 wt% by addition of Ni, due to the rehydriding reaction of LiH + Ni$_3$B$_3$ + 3/2H$_2$ $\rightarrow$ LiBH$_4$ + 2NiB. Weaker B-B bonding in Ni$_3$B$_3$ than that in elemental boron (icosahedral B$_{12}$ units) facilitates the rehydriding reaction. These results suggest that designing of systems similar to LiH/Ni$_3$B$_3$, in which boron atoms could move fast between two borides (e.g. Ni$_3$B$_3$ and NiB$_2$) during the reaction process, is expected to bring about improved reversible hydrogen storage properties.

**References**


Yigang Yan

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Rotational and Translational Diffusion in Calcium Borohydride from QENS and DFT Calculations[1]


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Metal borohydrides are of interest as hydrogen storage materials due to their high volumetric and gravimetric capacity. However, they are generally thermodynamically too stable, have slow absorption and desorption kinetics and poor reversibility. Noting the lack of knowledge about their structural transition and decomposition mechanisms we have investigated the hydrogen dynamics, using quasielastic neutron scattering, in calcium borohydride, and observed rotational and translational diffusion events.

In Ca(BH$_4$)$_2$ hydrogen dynamics can originate from long-range diffusion or localized motions (rotations, librations and vibrations). In this study, the rotational and diffusional dynamics of hydrogen were investigated by quasielastic neutron scattering (QENS) combined with Density Functional Theory (DFT) calculations. QENS experiments were performed with two spectrometers: SPHERES (Garching, Germany), energy resolution: 0.65 µeV, and MARS (PSI, Switzerland), energy resolution: 15 µeV. The DFT calculations were performed using the Atomic Simulation Environment package, the DACAPO plane wave basis set implementation and the Nudged Elastic Band method to calculate the energy paths of the re-orientational changes.

Rotational re-orientation

Between 95-280K, two thermally activated rotational motions were observed around the 2-fold (C$_2$) and 3-fold (C$_3$) axis of the BH$_4$ units. At the lower temperatures, only the C$_3$-rotation was detected while at higher temperatures a combination of the two rotations, with different characteristic times, was observed. The DFT calculated energy barriers were similar to the experimental ones (E$_{aC2}$= 0.15 eV and E$_{aC3}$=0.11 eV).

Long-Range Diffusion

Long-range diffusion events, with an energy barrier of E$_{aD}$=0.12 eV and an effective jump length of ~2.5 Å were observed at two temperatures with SPHERES. H jumps between two neighboring BH$_4^-$, diffusion of BH$_4^-$ and BH$_3$ groups were calculated and discarded due to their very high formation energies and diffusion barriers. Interstitial H, H$_2$, and H$_2$O diffusions were also calculated. H$_2$ interstitial diffusion gave results (0.09 eV, 2.1 Å) with the best agreement to the experimental values nevertheless, H$_2$O interstitial diffusion (~0.4 eV, <1.08 Å) couldn’t be strictly discarded. H$_2$ and/or H$_2$O interstitials might form during the synthesis of the compound.

Reference


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Reactive Hydride Composites

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Reactive Hydride Composites (RHC) release or store hydrogen by redox reactions between at least two hydrides. Upon desorption, components from both hydrides react exothermally, thus reducing the overall reaction enthalpy. Up to 11 wt.% hydrogen may be stored reversibly at technically relevant temperatures.

Reactive Hydride Composites

Reactive Hydride Composites like combinations of MgH\(_2\) with M(BH\(_4\))\(_x\) (M being Li, Na or Ca) show significantly reduced values of reaction enthalpies as well as improved ab- and desorption kinetics compared to the pure borohydrides.

Reaction Kinetics

In spite of a significantly lowered reaction enthalpy and thus high thermodynamic driving force for desorption, hydrogen release from LiBH\(_4\)/MgH\(_2\)-RHC still requires temperatures above 250°C. In this presentation, an overview will be given on reaction mechanisms, thermodynamic properties and sorption behavior of nanocrystalline RHCs: 2LiBH\(_4\)+MgH\(_2\), 2NaBH\(_4\)+MgH\(_2\) and Ca(BH\(_4\))\(_2\)+MgH\(_2\). Function and suitability of additives as potential catalysts on hydrogen ab- and desorption will be discussed and recent progress in optimizing reaction kinetics by nano-scaffolding will be presented.

System Integration

For application, suitable tank design is necessary to exploit the properties of newly developed hydrides. Key issues related to heat management and safety will be discussed.

References


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First Principles Prediction of Structural, vibrational and thermodynamic properties of Mixed Metal Hydrides and Fluorides

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Anionic substitution in high capacity metal hydrides still represents a promising route in the synthesis of novel materials for hydrogen storage applications. In the present work, fluoride anion was selected for the substitution and models of several F-substituted simple hydrides were simulated using DFT calculations, emphasizing a number of potential pitfalls encountered while modelling their thermodynamic properties.

Anionic substitution in hydrides

The aim of anionic substitution in high capacity metal hydrides is to destabilize thermodynamic properties of the too stable pure compounds by substituting some of the H atoms with halogens. The nature of the halogen plays an important role in the resulting thermodynamic properties of the mixed compound.

H/F substitution in simple hydrides

First of all, a complete characterization of structural, vibrational and thermodynamic properties of Li, Na, Mg, Ca and Al pure hydride has been carried out in the DFT scheme, using a Gaussian localized basis set and the periodic ab initio CRYSTAL09 code [1].

Once chosen the reference methodology (a reliable and feasible set of computational parameters), calculations for the following solid state reaction

\[(1-x)\text{MH}_n + x\text{MF}_n \rightarrow \text{MH}_{n(1-x)}\text{F}_x\]

were run and the mixed MHF compounds were carefully analyzed in terms of their properties.

In the present contribution, the focus will be mainly on Li, Na and Ca cases, since it has been recently demonstrated that for Al [2] and Mg no mixed structures resulted. For these hydrides, promising results have been obtained, but relevant differences were found in the thermodynamics depending on the specific modelling approach. Considering Ca(H,F) as a test case, for both the cubic and orthorhombic phases, potential pitfalls will be highlighted, to establish a sensible choice of the computational strategy.

References


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The Role of \( \text{Li}_2\text{B}_{12}\text{H}_{12} \) in the Sorption Cycle of \( \text{LiBH}_4 \)

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\( \text{Li}_2\text{B}_{12}\text{H}_{12} \) has been observed in the decomposition of \( \text{LiBH}_4 \) as well as a product in the reaction of \( \text{B}_2\text{H}_6 \) with \( \text{LiBH}_4 \), leading to a controversy whether \( \text{Li}_2\text{B}_{12}\text{H}_{12} \) is an intermediate or a by-product in the sorption cycle of \( \text{LiBH}_4 \).

**\( \text{Li}_2\text{B}_{12}\text{H}_{12} \) as by product**

By in situ X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) spectroscopy, we show that \( \text{Li}_2\text{B}_{12}\text{H}_{12} \) is formed in the gas-solid reaction of the sorption of \( \text{B}_2\text{H}_6 \) with \( \text{LiBH}_4 \) 200 °C (See Fig.1) [1].

![Fig. 1 Crystalline phase evolution during the reaction of \( \text{LiBH}_4 \) with diborane at 200 °C observed by in situ X-ray diffraction.](image)

\( \text{B}_2\text{H}_6 \) is also observed during the decomposition of \( \text{LiBH}_4 \) leading to the hypothesis that \( \text{Li}_2\text{B}_{12}\text{H}_{12} \) is a decomposition by-product, resulting from the reaction of \( \text{B}_2\text{H}_6 \) with residual \( \text{LiBH}_4 \).

**\( \text{Li}_2\text{B}_{12}\text{H}_{12} \) as intermediate**

By choosing the suitable conditions (\( \text{pH}_2 \), \( T \)), the decomposition of \( \text{LiBH}_4 \) can be forced to proceed via

\[
\text{LiBH}_4 \rightarrow 5/6\text{LiH} + 1/12\text{Li}_2\text{B}_{12}\text{H}_{12} + 13/12\text{H}_2.
\]

The thermal decomposition of \( \text{Li}_2\text{B}_{12}\text{H}_{12} \) itself leads to a further hydrogen release, so \( \text{Li}_2\text{B}_{12}\text{H}_{12} \) also occurs as an intermediate in the decomposition.

The role of \( \text{Li}_2\text{B}_{12}\text{H}_{12} \) obviously depends on the conditions of decomposition.

References


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Liquid Complex Hydrides

Andreas Züttel, Shunsuke Kato, Oliver Friedrichs, Andreas Borgschulte

Most known complex hydrides today are salt like solids and desorb the hydrogen only at elevated temperature. Liquid hydrides at room temperature in equilibrium with the hydrogen gas pressure of a few bar are preferable in view of mobile applications. Al[BH₄]₃ exhibits a volumetric hydrogen density of 150 kg/m³, melts at –60°C and spontaneously releases the hydrogen even below room temperature.

Liquid ionic compounds
The melting temperature of an ionic compound (salt) depends on the ratio of the diameter of the consisting ions. Partial substitution of the ions allows to stabilize phases and to change the melting temperature of a given ionic compound.

Stability
The complex hydride with a general formula of Mₓ[TH₄₋ₓ]ₓ (M = Li, Na, Mg, Ca…; T = Al, B, N and x is the stoichiometry) releases H⁻ to form MHₓ₋ₓ + x·TH₄⁻ [1]. The stability of the AlH₃ < BH₃ < NH₃, therefore, alanates decompose into hydrogen and aluminum while boranates tend to liberate beside hydrogen also B₂H₆ and the ammonium spontaneously decomposes into NH₃. Therefore, the thermodynamics i.e. stability and kinetics is calculated based on the intermediate products identified.

The stability of the TH₄⁻ is determined by the localisation of the electron on the T-atom. 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” TH₄ is also determining the equilibrium pressure of the complex hydride.

The empirical relationship between the enthalpy of formation and the electronegativity of the cation is linear [2]. The stability of the elemental hydride formed upon hydrogen desorption is given by the Pauling relation.

Therefore, the hydrogen desorption pressure as well as the melting temperature can be tailored by specific substitution of the anion and the cation in complex hydrides.

References

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Catalytic Combustion of Hydrogen on Platinum Coated Porous SiC Ceramics

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A self igniting catalytic hydrogen diffusion burner, based on porous ceramics with a platinum catalytic coating, has been developed for cooking and heating purposes in a novel autarky living unit. A very high passive safety measure is reached through the strict separation of hydrogen and air, the gases are mixed only on the catalytic coated SiC surface. Hazardous gases such as carbon monoxide, carbon dioxide, nitrogen monoxide and nitrogen dioxide are no issue.

The project focus is to develop a novel type of catalytic hydrogen burner. Highly porous silicon carbon foams coated with platinum are the basis of the development. Silicon carbide ceramics show excellent high temperature stability and thermal shock resistance. Platinum assures catalytic oxidation of hydrogen even at low surrounding temperatures. For safety reasons, the premix of hydrogen and air is avoided. While hydrogen is fed from below, defusing through the highly porous SiC foam, air is supplied to the upper SiC foam surface. Catalytic combustion thus mainly takes place inside the porous SiC structure.

2000°C, catalytic combustion allows such low combustion temperatures. Due to the high safety standard and easy power regulation, catalytic burners are favorable for safe indoor cooking and heating applications.

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Catalytic H₂ combustion, IR image at 900°C

H₂ flow vs heating values, ASP and Lambda value

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Gas-Solid Reactions for Heat Applications

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This paper gives an overview on current research projects at DLR concerning thermo-chemical heat storage. Additionally, a new possible application of an open metal hydride system to generate cold by utilizing the hydrogen pressure difference available in hydrogen driven cars will be presented.

Background

An efficient use of all available forms of energy is seen as one important path to a sustainable and payable future energy supply. In this context, efficient thermal energy storage is one key-factor that allows the utilization of e.g. intermittent solar thermal energy or industrial waste heat. Especially reversible gas-solid reactions are promising candidates for future heat storage systems as they offer high energy densities.

Operation Principle

The dissociation of a compound into two phases (gas, solid) by means of thermal energy can be used as heat storage if the products of the reaction are stored separately. The heat is released again if the two reaction partners are brought together. This principle is investigated at DLR for different temperature levels, ranging from around 500 °C (hydroxides) [1] for solar applications to lower temperatures (80 - 160°C) for industrial waste heat utilization (hydrates).

If the storage system is designed to operate in a closed mode (e.g. carbonates and hydrides) a separated storage for the gaseous compound is necessary. This has to be realized e.g. by mechanical compression of the gas but offers at the same time the possibility to transform heat as the reaction temperature can by controlled by means of the available pressure of the gaseous phase.

Application for Hydrogen Cars

Up to now the cost for materials reacting with hydrogen are too high to be competitive with e.g. carbonates or hydroxides for thermal energy storage. However, the fast reaction kinetics of metal hydrides at low temperatures together with the already available compressed gas storage offers a new application in future hydrogen driven cars.

The pressure difference between hydrogen tank and fuel cell can be used to generate a continuous cooling effect (sorption system), e.g. for onboard air-conditioning (Figure 1). As the compression work for hydrogen storage can be hereby partially re-utilized onboard, the overall energy efficiency of the car is increased. Additionally, conventional climate-damaging refrigerants (HFC) can be substituted.

References


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Hydrogen for Off-Grid Power Systems

Michael Bielmann, Ulrich Vogt, Andreas Züttel

Renewable off-grid power systems pose unique challenges for energy supply and management. The inherent absence of a demand-balancing grid has to be replaced with storage capacity on site. While currently this function is mostly accomplished by batteries, this approach offers severe drawbacks. Hydrogen based standalone power systems with on-site hydrogen generation offers opportunities to store large amounts of energy, add flexibility to the system and offer the ability for seasonal storage – a function that cannot be accomplished by batteries alone.

Challenges in renewable off-grid power supply
In off-grid renewable energy supply systems, demand and supply of energy is highly fluctuating. In contrast to traditional approaches, energy production by PV or Wind are not under direct control. Therefore, the balancing and matching of demand and supply has to be an inherent functionality of the system itself. Traditionally, this function is served by lead-acid batteries. Therefore, the amount of energy harvested is always a parameter of the available storage capacity, which is – depending on the situation – severely limited by volume and mass constraints. Especially PV pose a tough challenge – the seasonal variation of production cannot be serviced by battery systems, making a large overdesign of the PV system a necessity. The necessary large capacities cannot be offered by batteries which suffer from self-discharge and low energy density.

Hydrogen for seasonal storage
Hydrogen offers the unique opportunity energy densities unachievable by any battery technology. Using excess energy to produce hydrogen for seasonal storage on-site is therefore the perfect best of both worlds approach, where batteries offer short term storage and power capability while hydrogen through electrolysis, storage and fuel cells add long term capabilities to the system. This approach will be discussed in detail by the practical example of SELF, a self-sufficient living unit and technology platform developed by EMPA.

References

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Monte Carlo calculations of the free energy of SII and SH clathrates

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Clathrate hydrates are crystalline molecular compounds composed of a water host lattice and guest molecules. To stabilize the compounds, the guest molecules called promoters are entrapped into cavities of the host water structure. Clathrate hydrates are of great technological interest for hydrogen storage because of their capacity to store gas at relatively high density and therefore considered as prospective candidates for hydrogen storage materials [1]. Studies of free energies of gas hydrates are important to explore stability, i.e. to find the most effective promoters, and to compute phase diagrams. Recently developed self-referential (SR) method [2] for computing the free energy of crystals composed of rigid nonlinear molecules is based only on the knowledge of intermolecular potential. In this work the SR technique was applied to calculate free energy of sII and sH clathrates with cavities occupied by hydrogen molecules and different promoters.

References


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Annealed GdC Thin Films Microstructure Evaluation

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Solid oxide fuel cells (SOFC) are considered a promising power generation technology. Gadolinia-doped ceria (GDC) is an alternative electrolyte material which offering the possibility of lower temperature SOFC operation (500°C ÷ 700°C). Magnetron sputtering is a well-developed, promising, flexible deposition technique for preparing thin electrolytes of GDC. By this technique the layers are deposited from the atomic phase; for this reason deposited films do not need annealing at high temperatures.

Thin films formation

The method of nano-crystalline thin films formation can greatly affect on the nanostructure and overall performance properties of GDC. The quality of such thin films depends on structural peculiarities, which are influenced by the technological parameters of formation methods [1, 2].

Microstructure

Firstly Ce$_{x}$O$_{y}$, then Gd$_{x}$O$_{y}$ multilayer sandwich systems with 6 and 12 layers were made by reactive magnetron sputtering in reactive O$_{2}$/Ar gas mixtures. Increasing number of the layers, taking in mind that a Ceria must be 90 at.% and Gadolinia – about 10 at.%, were included to the general thickness (~600 nm) of the films. These multilayer systems were annealed at 600°C and 700°C temperature in air. X-ray diffraction studies and SEM analysis of GDC (Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$) thin films were studied there. The calculation of texture coefficients showed the crystallized cubic fluorite structure with orientation (111) of 6 and 12 layers at 600°C and 700°C annealed temperatures. The highest value of texture coefficient $R=0.901$ was obtained for 12 layers system annealed at 700°C. The best ionic conductivity of this GDC structures orientation is contemplated. It was found that the crystallite size of 12 layers GDC thin films increased about 50% after annealing in 700°C temperature (~12 nm) comparing with 600°C annealing temperature (~8 nm). From this work is shown that gadolinia-based ceria thin films with applicable properties could be formed using magnetron sputtering.

References


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Characterization of Commercial Metal-Oxide Ceramic Diaphragms for Hydrogen Production by Alkaline Electrolysis

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Commercial metal-oxide ceramic diaphragms for hydrogen production by alkaline electrolysis were tested in a lab-scale electrolyzer at ambient conditions for over-potential and gas purities. Additionally, the specimens were characterized structurally by SEM (scanning electron microscope), XRD (X-ray diffraction), and RS (Raman spectroscopy) and electrochemically by EIS (impedance spectroscopy). Short time corrosion tests at various concentration of KOH were performed.

Introduction

Conventional alkaline electrolysers with zero-gap cell geometry operate at 85°C, 32 bars and use 25 wt% KOH as electrolyte. Asbestos diaphragms, used as ion-permeable separator, prevent intermixing of produced H₂ and O₂ gases. Hydrogen produce by this technology has a purity in range of 99.98 - 99.99% [1]. Due to health regulations but also low chemical stability at temperatures above 100°C, the replacement of ion-permeable asbestos diaphragms essential.

Experiments

Composite ceramics (CMCs), based on Nextel 610 fibers as reinforcement and mixture of Al₂O₃/8-mol% Y₂O₃ doped ZrO₂ as matrix, were tested in lab electrolysis- and impedance cells with current density of 200 mA.cm⁻². The characterization of the diaphragms focused on ion-conductivity, porosity, structural and surface changes. The chemical stability in KOH of 25 wt%, 30 wt% and 50 wt%, respectively, at 85 °C was determined by gravimetric analysis. The density and porosity was determined by Archimedes method. Structure characterization and its changes were obtained by conventional scanning electron microscopy, X-ray diffraction technique and Raman spectroscopy.

References

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Architecture of Air Independent Electric Supply System Based on PEM Fuel Cell

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PEM fuel cell systems have to be supplied from hydrogen and oxygen sources. In most cases, oxygen is achieved from ambient atmosphere and hydrogen is stored in pressurized tanks, metal hydrides storages or chemically bounded in other chemical compounds. Unfortunately, in some cases e.g. during underwater operation, oxygen is not accessible. Then, both hydrogen and oxygen have to be stored and fuel cell system has specific oxygen supply subsystem.

Introduction
An Air Independent Electric Supply System AIESS based on PEM fuel cell was built in Polish Naval Academy. The system can work in underwater conditions and is supplied by both clean hydrogen and clean oxygen stored in pressurized tanks [1].

Architecture of AIESS
AIESS was built in the Laboratory of Electric Drives to demonstrate application of PEM fuel cell technology in supplying underwater platforms. The Air Independent Electric Supply System consists of:
1) PEM fuel cell system with nominal power 6 kW based on P8 stack from Nedstack Company, Arnhem, Netherlands,
2) DC/DC converter stabilizing voltage at level 220 V, connected in parallel with supercapacitors,
3) an electric load consisting of: an electric motor, a lighting set and a heating,
4) installations and pressured tanks of oxygen, hydrogen and nitrogen.

The PEM fuel cell system is controlled by S7-300 PLC. The controller is connected with a touch panel and PC through MPI protocol. The touch panel performs Human Machine Interface, whereas PC visualizes operation and registers parameters of the system.

Results
Based on achieved results of operation AIESS [1], the PEM fuel cell system responds on changes of an electric load (about 50 A) in short time (about 3 seconds) with small over-regulation (about 2 V).

References

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Dynamic Modeling and Simulation of Anode-Supported Planar Solid Oxide Fuel Cell

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To explore the dynamic characteristics of the SOFC system and to develop relevant control strategies, a reduced-order dynamic cell model developed for planar solid oxide fuel cells, based on existing and improved models. Applying two control strategies, the cell model is implemented to analyze the dynamic behavior of an anode-supported SOFC cell. The results show that the relaxation time is strongly related to the thermal behavior of the cell and the applied control strategy.

Introduction

Dynamic studies and development of suitable control strategies are key tasks for realization of the SOFC systems. Therefore, the main focus of the present research was developing a computational model to explore the dynamic characteristics of the SOFC cell and to develop control strategies that can ensure fast and safe transient operation.

Method

Based on the above goals, a reduced-order dynamic cell model developed for the planar solid oxide fuel cell, based on existing and improved models, comprising the mass, momentum, energy and electrochemical analysis as well as a kinetic model of hydrocarbon reactions. The electrochemical model includes a complete evaluation of ohmic, activation and diffusion losses. In comparison to the most previous literature models, dynamic terms have been implemented in both energy and mass conservation equations. To verify the model, it is compared with available experimental and benchmark test data as well as some previous numerical results, showing the capacity of the model to accurately predict the SOFC operating conditions. The cell model is applied to analyze the dynamic behavior of an anode supported SOFC cell caused by step load changes based on two control strategies i.e. cell constant fuel flow rate and constant fuel utilization during the load variation. The effect of several parameters e.g. interconnector materials, load variation magnitude, has been investigated.

Results

The results show that the relaxation time is strongly related to the thermal behavior of the cell as well as the applied control strategy and cell material properties. However, it is almost independent of the load variation magnitude.

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First-Principles Calculations of Hydrogen Diffusion into Palladium Nanoparticles

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In this research, density functional theory (DFT) calculations for the surface adsorption and subsurface absorption of hydrogen on Palladium clusters are performed. We investigate the hydrogen-site specific effects and how the hydrogen storage properties of Pd clusters change with the cluster size. The hydrogen diffusion barriers are calculated for interstitial sites, from the surface to the subsurface of Pd clusters and compared to those of bulk and Pd (111) surface systems, which can provide us an interpretation of the stability of the hydrogenated Pd clusters.

Hydrogen Storage by Palladium Nanoparticles

Pd is an archetypical hydrogen storage metal and stores hydrogen under ambient conditions. The hydrogen storage properties of Pd nanoparticles vary depending on the particle sizes and the stabilizers [1]. The hydrogen solubility and equilibrium pressure for the formation of palladium hydride decrease with a decrease in the particle size. Hydrogen is also known to adsorb strongly on the surface of Pd clusters, thereby greatly changing the structure of the clusters.

Computational Method

The density functional theory calculations were performed using the VASP code with PAW pseudopotentials to describe the electron-ion interaction. The nudged elastic band method was used to find the minimum energy path and the corresponding energy barriers for hydrogen diffusion process.

Hydrogen Diffusion into Pd Icosahedral clusters

To examine the possibility of the diffusion of a H atom from the surface into the subsurface of Pd icosahedral clusters, we estimated the energy barriers for H migrating from the surface to the subsurface and the migration energy of H between the interstitial sites inside clusters. The energy profiles along the H diffusion paths in Pd clusters are presented. The results were compared to those of (111) surface [2]. We suggest that chemisorbed H occupies both surface and subsurface sites of Pd clusters.

References

Investigation of the Hydrogen Sorption Properties of Nanocomposites NaBH₄-MgH₂ Confined into Mesoporous SBA15

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In the field of hydrogen storage materials, recent results underline improved sorption properties of nanosized powders with grain size lower than 20 nm with respect to the conventional bulk materials. The reduction to nanometer scale and the control of grain size of hydride particles, obtained through the confinement within nanoporous-scaffolds, appear to have beneficial effects on the thermodynamic properties and kinetics of hydrogen release and uptake. Along this line in this work we focus on the hydrogen sorption properties of NaBH₄-MgH₂ system embedded into Si-based mesoporous matrix, SBA15, by wet chemical or by melting impregnation methods. Moreover, the pore network of the hosting material, controlling the particle size of the active phases, could facilitate the interaction between the hydrides during the ab-desorption process. Different hydride stoichiometries were investigated and different additives were tested. Microstructural characterization of samples was performed by diffraction, calorimetric and microscopic techniques, while the hydrogen ab-desorption properties were studied by using gravimetric volumetric techniques as well as by thermal desorption spectroscopy analyses.

Chiara Milanese (born in 1974) graduated in Chemistry cum laude at the University of Pavia, Italy, in 1998 and she took her PhD in Chemical Sciences in 2002. Subsequently, she obtained a post doc grant focused on the preparation and characterization of materials for energetics. Since 2008 she has been researcher at the Faculty of Pharmacy of the University of Pavia. Starting from the same year, she has been the technical responsible of the Pavia H₂ Lab. She is working on Mg – based materials and MgH₂ – borohydrides systems.

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The new complex hydride, Li$_3$(NH$_2$)$_2$I, with an unique crystal structure was synthesized, and then the ion conductivity was experimentally studied.

**Lithium Fast-Ion Conductivity in Li(BH$_4$)$_3$**

The ion conductivity of Li(BH$_4$)$_3$ increases by three orders of magnitude at 390 K due to its structural transition from the orthorhombic low-temperature (LT-)phase to the hexagonal high-temperature (HT-)phase. From the application point of view, it is highly desirable to enhance the conductivity of Li(BH$_4$)$_3$ at RT.

**Enhanced Conductivities in Li(BH$_4$)$_3$–LiX (X = Cl, Br, and I) and Li(BH$_4$)$_3$–Li(NH$_2$)$_2$**

The enhanced conductivities in Li(BH$_4$)$_3$–LiX and Li(BH$_4$)$_3$–Li(NH$_2$)$_2$ have been demonstrated. In Li(BH$_4$)$_3$–LiI, the HT-phase of Li(BH$_4$)$_3$ can be stabilized below 390 K by forming solid solution phase with a wide range of compositions; as a result, the conductivity (4 × 10$^{-5}$ S/cm) becomes three orders of magnitude higher than that of pure Li(BH$_4$)$_3$ (2 × 10$^{-8}$ S/cm) at RT. In the case of Li(BH$_4$)$_3$–Li(NH$_2$)$_2$, Li$_2$(BH$_4$)(NH$_2$)$_3$ both with combinations of [BH$_4$]$^-$ and [NH$_2$]$^-$ complex anions, show fast-ion conductivities of 1 × 10$^{-4}$ S/cm at RT because of new occupation sites available to Li$^+$ ions. These experimental results suggest that various fast-ion conductors may exist in the Li(BH$_4$)$_3$–Li(NH$_2$)$_2$–LiI system.

**New Complex Hydride in Li(BH$_4$)$_3$–Li(NH$_2$)$_2$–LiI: Conductivity?**

The new complex hydride, Li$_3$(NH$_2$)$_2$I, with an unique crystal structure was synthesized. The experimental result on its conductivity will be explained in the presentation.

**References**


Conceptual Approach to New metal-organic Frameworks for hydrogen Storage

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Two Zn MOFs, MOF-645 and MOF-646, comprised of polarized 1,3-azulenedicarboxylate were synthesized. The guest free MOF-646 showed strong MOF-H$_2$ interactions (7.8 – 6.8 kJ mol$^{-1}$), which revealed the significant impact of internally polarized azulene backbone to stabilized H$_2$ molecules in the framework.

Polarized binding of dihydrogen

In the last few decades an extensive research focus have been devoted towards finding a suitable Porous Coordination Polymers (PCPs) or Metal–Organic Frameworks (MOFs) as an on-board hydrogen storage system.[1] Based on theoretical and experimental studies it has become pertinent that the increase in the binding energy of the materials up to 15-20 kJ/mol is the most crucial step towards designing the ambient temperature storage systems.[2]

Azulenes constitute dipolar aromatic systems and we anticipated that these contained in a MOF could contribute to build up of cumbic fields required for the polarization and polarized binding of H$_2$. [3] Therefore, we strived to prepare MOFs namely MOF-646 $[\text{Zn}_3\text{O}\text{net}]_3$ (lcy net) and MOF-645 $[\text{Zn}_5\text{(OH)}_2\text{net}]_4$ (bcu net) comprised of polarized angular 1,3-azulenedicarboxylate and Zn$^{2+}$. Indeed, the guest free MOF-646 demonstrates excellent volumetric H$_2$ uptake of 20.9 g L$^{-1}$ at 77 K and 1 bar, and more interestingly the isosteric heat of adsorption was as high as 7 kJ mol$^{-1}$ even at 13.3 mg g$^{-1}$ of H$_2$ loading.[4] This reveals the significant impact of internally polarized azulene backbone to stabilize H$_2$ molecules in the framework.

References


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New Double-Cation Borohydrides

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Conventional borohydrides are not meeting the thermodynamic requirements for hydrogen storage materials used in mobile applications. It is the aim to adjust their stability by combining two different cations forming novel double-cation borohydrides. Al-Li-borohydride (17.2 wt.% H₂) and Al-Na-borohydride (14.6 wt.% H₂) were synthesised by metathesis reaction during ball milling. Their decomposition occurs around 70°C and 90°C, respectively. Decomposition pathways were analysed by means of in-situ Raman spectroscopy.

Introduction

The stability of borohydrides is dependent on the electronegativity of the cation [1]. In order to meet stability requirements for hydrogen storage materials two cations with very different electronegativity are combined to form a double-cation borohydride with intermediate stability. NaBH₄ is more stable than LiBH₄ therefore decomposition should occur at higher temperature for Al-Na-borohydride than for Al-Li-borohydride. Li et al. [2] did a similar milling of AlCl₃ and LiBH₄ which showed decomposition around 70°C. We did further investigation on that and compared it also with another system using NaBH₄.

Synthesis and Structure

The two double-cation borohydrides Al-Li-borohydride and Al-Na-borohydride were synthesized by metathesis reaction. Either AlCl₃ and LiBH₄ or NaBH₄ were ball milled for 5h in Ar atmosphere in different molar ratios. Structural analysis was done by XRD and Raman spectroscopy. Collected synchrotron data was used for structure determination backed up by DFT-calculation. Al-Li-borohydride showed a very different structure than expected in the literature. It forms a primitive cubic unit cell consisting of complex cations [Li₄(BH₄)]³⁺ and anions [Al(BH₄)₄]⁻. Na-Al-borohydride contains only complex anions and shows an orthorhombic structure.

References


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Hydrogen Storage in Carbon Cones

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Large scale production of conical carbon nanostructures (so-called carbon cones) [1] that are fundamentally different from the other nanocarbon materials, such as buckyballs and nanotubes, can be made using the so-called Kvaerner Carbon Black & Hydrogen Process [2]. This involves pyrolysis of hydrocarbons using a torch plasma process. The carbon cones that occur appear in five distinctly different forms. Earlier reports indicated that these structures exhibit unusually high H2 uptake and release at room temperature not known in other forms of carbon [3]. Here we report about the recent progress of the experimental research and theoretical modelling of these cluster particles with emphasis on H2 storage.

References:


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Hydrogen Processing / recycling of rare earth magnets

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Rare earth magnets such as NdFeB are strategically important materials for many clean technologies. The Chinese completely dominate the rare earth market supplying around 97% of the world’s rare earth metals. This is causing considerable concern in the EU, US and Japan. The house of representatives in Washington recently approved a bill authorising research to address the supply of rare earths, saying the minerals were critical to energy, military and manufacturing technologies [1]. The Magnetic Materials Group at the University of Birmingham has been investigating the use of hydrogen to reprocess / recycle NdFeB magnets. This work outlines the case for recycling rare earth magnets and gives an overview of the research activities which have been carried out to date.

Introduction

China produces approximately 97% of the world’s rare earth elements including neodymium and dysprosium. Rare earth mining/refining processes are environmentally damaging as these activities are energy intensive and develop waste products such as fluorine, radioactive thorium, sulphuric acid, hydrofluoric acid and dust. Nd and Dy are used in rare earth magnets which are strategically important for a huge number of modern day applications including for example motors in electrical vehicles, generators in wind turbines and small electronic devices such as mobile phones and hard disk drives. Chinese demand for Nd is expected to outstrip its own production in the next few years and they have already begun restricting exports to the rest of the world [2]. In the last twelve months Nd prices have risen from ~20$/kg to ~100$/kg. Given the strategic importance of these elements, the market dominance of China and the environmental damage caused by mining these materials, there is a very strong argument for recycling existing scrap NdFeB magnets.

Hydrogen is already employed commercially to produce NdFeB magnets by breaking up cast NdFeB into a powder (HD process) [3]. Hydrogen is initially absorbed by the Nd rich grain boundary phase (at RT and atmospheric pressure) with an associated volume expansion. This results in the material breaking into a powder, which can easily be jet milled and then pressed to produce sintered NdFeB magnets. In this work, the HD process has been employed to re-process and recycle existing sintered NdFeB magnets into a powder which can be used to produce new magnets [4].

References


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KINETIC AND THERMODYNAMIC INVESTIGATIONS ON PURE AND DOPED NaBH$_4$ – MgH$_2$ SYSTEM.

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In this work, NaBH$_4$ – MgH$_2$ mixtures with 2:1 and 1:2 molar ratio have been deeply investigated by thermal programmed desorption (TPD) runs and coupled manometric – calorimetric analyses in order to describe the Mg/MgH$_2$ effect on the kinetics and thermodynamic of NaBH$_4$ desorption. A mechanistic hypothesis on this complex process has been drawn and the dissociation enthalpy of the compound in the binary systems has been obtained. Moreover, the catalyzing/destabilizing effect of different additives (fluorides, chlorides, hydroxides, fluoroborates) has been studied. The best results have been obtained for MgF$_2$ concerning the 2:1 stoichiometry.

**Introduction**

The NaBH$_4$ – MgH$_2$ system has gained attention in the last few years as possible hydrogen storage system thanks to its high theoretical gravimetric capacity (10.7 wt%), low cost (less than 1 € for each kg) and the higher stability of NaBH$_4$ with respect to the other borohydrides. The challenges are to find good catalyzing/destabilizing agents in order to make the decomposition of NaBH$_4$ contemporary to that of MgH$_2$ and to achieve fully reversibility for the system.

**Experimental**

NaBH$_4$ + MgH$_2$ binary mixtures with 1:2 and 2:1 molar stoichiometry and ternary mixtures added with 0.05 mol of dopants (fluorides, chlorides, hydroxides, fluoroborates) were milled under Ar for 20 h by a planetary mill in a stainless steel vial with a 10:1 balls to powders ratio. TPD and coupled manometric – calorimetric measurements up to 600 °C @ 0.1 bar H$_2$, combined with ex – situ X-ray powder diffraction analysis, allowed to obtain details on the kinetics and thermodynamics of the different decomposition steps.

**Results**

For all the mixtures, MgH$_2$ dehydrogenation takes place at temperatures much lower than NaBH$_4$ decomposition (the differences being up to 140 °C). For the 2:1 composition, this last process takes place in the wide range between 450 °C and 550 °C, where the melting temperature of NaBH$_4$ (505 °C) is comprised. A melting/decomposition mechanism, driven by MgB$_2$ formation, is proposed, with the decomposition enthalpy of NaBH$_4$ (90 kJ/mol H$_2$) decreased of about 18 kJ/mol H$_2$ with respect to the pure compound. For the 1:2 stoichiometry NaBH$_4$ decomposition ends at about 490 °C, so involving only solid phases, and it appears thermo-dynamically less favourable. Among the tested dopants, for the 2:1 stoichiometry, MgF$_2$ appears effective in both reducing the temperature lag between the decomposition of the hydrides and improving the sorption thermodynamics and kinetics.
An IAEA Insight of Activities on Hydrogen Production

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Current energy demand keeps increasing worldwide especially in China and India. This demand has been met so far primarily by burning fossil fuel. As hydrogen is being considered as the replacement of fossil fuel, the viability of hydrogen economy is becoming more feasible. The use of nuclear energy for commercial hydrogen production is predicted to play a major role in future. The potential of hydrogen production using nuclear energy has lead the IAEA to carry out an active programme on the nuclear hydrogen production. The programme includes meetings for information exchange on status of nuclear hydrogen production, future challenges to nuclear hydrogen production with emphasis on safety of coupling, future aspects of hydrogen economy, and very recently the development of the hydrogen economic evaluation software HEEP for nuclear hydrogen production.

In addition to presenting a summary of the IAEA activities on nuclear hydrogen production and some details of the IAEA HEEP software which is developed mainly for the evaluation of the economic assessment of the hydrogen economy, the paper will highlight some insights from recent activities covering major conclusions presented by participants from some Member States which are very active on nuclear hydrogen production.

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Magnesium fullerides for hydrogen storage

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Abstract: The successful intercalation of magnesium in the lattice of $C_{60}$ obtained by different preparation procedures opens to the possibility of employing these new materials for the storage of hydrogen. The $H_2$ molecule interaction with both charged $C_{60}$ and magnesium ions can fall into the useful energy range to achieve a reversible $H_2$ storage at room temperature.

Hydrogen in fullerenes

Many recent theoretical works indicate the class of metal doped fullerene compounds as very promising for hydrogen storage [1]: on the one hand, the calculated binding energy of hydrogen on a curved graphene plane should be enhanced by increasing its curvature; on the other hand, DFT calculations predict a further relevant increase if fullerenes are in a charged state. Moreover, the metal ion (i.e. Ca$^{2+}$ and Mg$^{2+}$) could play an important role in optimising the hydrogen binding energy to the 20-40 KJ/mol useful value, either by a charge-induced polarisation, or even by a partial hybridisation of the hydrogen molecular orbitals (Kubas interaction [2]). However, a systematic study of these systems is still missing, especially due to the difficulties inherent the preparation of these materials.

Mg$_x$C$_{60}$ compounds

In this work we focus on magnesium intercalated fullerenes. On the one hand, the smallest alkali-earth atoms are expected to donate two electrons each to the $C_{60}$ molecule and stabilise a charge transfer salt thus preventing the formation of Mg clusters. On the other hand, the Mg$^{2+}$ valence orbitals could mix with the bonding and anti-bonding $H_2$ orbitals, thus modifying the H-H bond length. This interaction (Kubas interaction) was shown to be attractive and in the proper energy range for applications for the storage of hydrogen. We managed to prepare various Mg fullerides with different composition and structure. Their synthesis was achieved either through solid state reactions (also using metallorganic precursors) or in solution. Measurements of $H_2$ absorption efficiency are now in progress.

References


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Hydrogen Storage Properties of LiBH$_4$-based Reactive Hydride Composites

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Among complex metal hydrides, lithium borohydride (LiBH$_4$) has recently received great attention as a solid-state hydrogen storage material owing to its high gravimetric hydrogen storage density. LiBH$_4$ is known to decompose into LiH and B, releasing 13.9 wt% hydrogen. In this talk, hydrogen storage properties of LiBH$_4$-based reactive hydride composites are presented.

Dehydrogenation behavior of 6LiBH$_4$ + CaH$_2$ composite has been investigated. The composite starts dehydrogenation before the melting of LiBH$_4$ and releases 9.1 wt% hydrogen up to 400 °C. The equilibrium dehydrogenation temperature under 1 bar of hydrogen is estimated to be 309 °C with a reaction enthalpy change of 56.5 kJ/mol H$_2$, which is consistent with thermodynamic calculation. Rehydrogenation behavior of the composite has been studied between 350 and 500 °C after dehydrogenation at 450 °C. The composite exhibits the best rehydrogenation feature at 450 °C in terms of the overall rehydrogenation rate and the amount of absorbed hydrogen. It is found that about 9 wt% hydrogen is absorbed at 450 °C for 12 hours. Up to 10 dehydrogenation-hydrogenation cycles have been carried out for the composite. It is demonstrated that 6LiBH$_4$ + CaH$_2$ with 15 wt% NbF$_5$ maintains a reversible hydrogen storage capacity of about 6 wt% at 450 °C after a slight degradation between the 1st and 5th cycles.

Hydrogen back pressure remarkably promotes the formation of metal boride during the dehydrogenation of 4LiBH$_4$ + YH$_3$, 6LiBH$_4$ + CeH$_2$ and 6LiBH$_4$ + CaH$_2$ composites, which seems to be a general phenomenon in LiBH$_4$-based reactive hydride composites that enables mutual destabilization between LiBH$_4$ and metal hydride. The formation of metal boride plays a crucial role in the reversible hydrogen storage properties of these composites. The dependence of the dehydrogenation behavior on hydrogen back pressure might be associated with the microstructural evolution of the dehydrogenation products formed by a solid-liquid reaction.

References


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CONTROL OF OXYGEN FLOW IN AIR INDEPENDENT PEM FUEL CELL SYSTEM

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More often, hydrogen fuel cells are used to supply different devices and vehicles both for civilian and military applications. One of the more popular hydrogen fuel cells are low-temperature PEM (Proton Exchange Membrane). In the case of using them in conditions without access to air e.g. underwater conditions, it is necessary to deliver to a fuel cell both hydrogen and oxygen.

Introduction

An Air Independent Electric Supply System AIESS based on PEM fuel cell was built in the Polish Naval Academy. The system can work in conditions without access to air e.g. under the surface of sea. The fuel cell is supplied by both clean hydrogen and clean oxygen stored in pressurized tanks. The whole air independent system is described in [1].

Structure of oxygen supply subsystem

Opened-loop structure of oxygen supply subsystem was used in AIESS. This type of subsystems releases an excess of oxygen to an ambient environment. The excess can be consumed by a crew e.g. on a board of a submarine. In this case, it is necessary to control a flow of an oxygen very carefully and precisely.

The oxygen supply subsystem consists of several elements, carrying out proper flow rate and humidification of an oxygen. The main device is a flow controller. The Bronkhorst F-201 flow controller was used as a main element of oxygen supply subsystem.

Results

The results of a control of an oxygen flow were presented in detail in [1][2]. Good response of the system on changes of an electric load was achieved by means of Bronkhorst flow controller with implemented PID controller. Moreover, a safe level of oxygen excess was registered. Maximal registered value of the oxygen excess (1,5 NL/min) corresponds to quantity of oxygen consumed by 4-5 people (the crew has 20 and more people).

References


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Hydrogen Storage in Structure II Clathrate Hydrates with Various Promoters

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Hydrogen ($H_2$) is a promising alternative to fossil fuels, because it offers a solution for three main global challenges: (i) reduction of greenhouse gas emissions, (ii) fulfillment of energy requirements and (iii) reduction of local air pollution. However, due to the difficulty in finding an effective storage medium, the application of $H_2$, for instance in the automotive sector, is currently limited. Clathrate hydrates, have been regarded as a favorable alternative for $H_2$ storage. Their profitability, safety, fast and high reversibility and efficient production make them more suitable for this application than other $H_2$ storage materials.

Clathrate hydrates are a class of crystalline inclusion compounds, where water molecules form cavities that can host suitable guest molecules. The guest molecules are typically gases or volatile organic compounds, which fill the cages and stabilize the hydrate structure. Depending on the size and properties of the guest molecules, clathrate hydrates may occur in three different crystal structures: (i) structure I ($sI$), (ii) structure II ($sII$), and (iii) structure H ($sH$). $H_2$ clathrate hydrates, exhibit a structure II ($sII$) configuration, where 136 water molecules form sixteen small cavities and eight larger ones. Such material exhibits a storage capacity of 5.0 wt % of $H_2$ at extremely high pressures, i.e. in excess of 200 MPa. The addition of a second type of guest molecule, a so-called “promoter”, reduces the formation pressure two orders of magnitude, by means of forming mixed $sII H_2 +$ organic clathrate hydrates. However, the addition of a promoter significantly reduces the $H_2$ storage capacity (close to 1.1 wt%). In order to be considered practical, clathrate hydrates should have sufficiently high $H_2$ storage capacity (> 5 wt%) at relatively mild temperature and pressure conditions.

Motivated by this, five new promoters for mixed $sII H_2$ clathrate hydrates were studied. These promoters are known to form $sII$ clathrate hydrates with water. The incorporation of these potential promoters into the $sII H_2$ clathrate hydrates decreases the necessary storage pressure. The results from this study may also elucidate the relation between the properties of the promoter molecules and the mixed $H_2$ clathrate hydrates stability.

Dr.ir. Cor J. Peters earned his bachelor (cum laude), master (cum laude), and Ph.D. degrees from Delft University of Technology in the Netherlands. Dr. Peters is an expert in the areas of thermodynamics, phase equilibria, ionic liquids, hydrogen storage, gas hydrates and CO$_2$-sequestration. For the period 2002-2006 he was appointed as a visiting professor at the Center of Excellence of Tohoku University, Sendai, Japan. Dr. Peters has worldwide extensive collaborations. His current collaborations comprise Stanford and Vanderbilt University, University of Maryland, Colorado School of Mines, all of them in the USA. In addition, he has strong ties with the Center of Excellence at Tohoku University (Japan), the Universidad Nacional del Sur (Argentina), University of Nottingham (UK) and the University of Valladolid (Spain). He is Distinguished Professor of Chemical Engineering at the Petroleum Institute in Abu Dhabi, United Arab Emirates.

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Gas Separation Diaphragms for Alkaline Hydrogen Production: Influence of Microstructure on Ion Conductivity and Gas Purities

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High purity of hydrogen produced by high-pressure alkaline electrolysis is ensured by a porous and ion conductive diaphragm separating anode and cathode of an electrolysis cell. In order to keep the cell resistance low, the ionic conductivity of the porous diaphragm is crucial. Thereby, the conductivity is related to the pore structure. In this study we characterize the pore structure of different diaphragms by means of multi scale tomography and establish a link to the electrochemical cell performance.

Introduction

Until today, flexible asbestos tissues are used in alkaline electrolysis, as they show good ion conductivity and easily can be installed between the electrodes without being damaged. Due to recent health regulations, asbestos based diaphragms are prohibited in new electrolysers. For the development of alternative material concepts, a thorough understanding of the link between microstructure and cell performance is fundamental.

Experimental

Different sets of porous diaphragms made of different materials were tested in a lab scale electrolyser regarding cell voltage and purity of the produced gasses hydrogen and oxygen. To establish a link between diaphragm pore structures, ion conductivity, and gas purity, the diaphragms were structurally and electrochemically characterized by different methods. The combination of standard electron microscopy with low voltage FIB-nanotomography [1] and synchrotron-microtomography resolves the pore structure of the asbestos reference diaphragms and new developed diaphragms. Based on modern imaging analyses techniques, the 3D pore structures are described quantitatively. Reference asbestos diaphragms consist of a dense solid material, large micro-pores and dense matrix material with reduced permeability [2]. The influence of ion conductivity regarding the electrochemical performance is characterized by impedance spectroscopy [3].

References


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REDUCTION TEMPERATURE IMPACT ON NiO-YSZ CERMETS MICROSTRUCTURE

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Cermet coatings of yttria stabilized zirconia with nickel (YSZ-Ni) are the most promising for the anode-supported solid oxide fuel cells (SOFC). It is necessary to define the hydrogen reduction process, where NiO converts to Ni, in order to achieve optimized initial microstructure of the NiO-YSZ cermets. In this study, the influence of hydrogen reduction temperature on NiO-YSZ cermets prepared by screen-printing method has been investigated.

Experimental procedure

The screen-printing technology was used to produce NiO-YSZ cermets by mixing NiO and YSZ powders in variable composition ratio from 35%-65% to 70%-30% with 5% increments. NiO-YSZ powders were mixed with suitable organic additives and printed on Al₂O₃ substrate. A 18 μm thick cermets were then calcined at 1350 °C for 2 h. Hydrogen reduction on NiO-YSZ anodes was investigated at 300 °C, 600 °C, 800 °C and 1000 °C reduction temperatures for 1 h.

Microstructure

The reduction procedure is crucial to the initial anodic microstructure, while initial anodic microstructure influences the performance of the anodic cell. The microstructure, elemental composition of unreduced and reduced NiO-YSZ cermets with different porosity was analyzed using scanning electron microscope (SEM) and X-ray energy dispersive method (EDX).

X-ray diffraction (XRD) method was employed to indentify and quantify the phases of anodic cermets before and after the reduction. It was found that NiO-YSZ cermets consist mainly of cubic yttria stabilized zirconia and nickel oxide phases and additional cubic nickel phase resulting from NiO to Ni during the hydrogen reduction.

In addition to changes in the chemical composition of NiO-YSZ cermets during reduction, the porosity of the anodes was changed as well. This was expected since the specific volume of metallic Ni after reduction was significantly smaller than that of NiO [1].

As a result of hydrogen reduction, the porosity increase is clearly demonstrated.

References


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METHANE PRODUCTION THROUGH HYDROGEN FROM RENEWABLE ENERGY

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It is natural that all people in the whole world wish to consume at least the same amount of energy as the average amount of energy consumed by a person in developed countries. Thus, the continuation of the current energy supply system will lead to complete exhaustion of the world reserves of all fossil fuels and uranium until the middle of this century. The technology to supply fuels produced from renewable energy, by which all people in the whole world can survive without using fossil fuels, should be urgently established. The technology presented here is to supply renewable energy in the form of methane using carbon dioxide as the feedstock by the reaction with hydrogen produced by seawater electrolysis.

We are proposing global carbon dioxide recycling. The electricity necessary for all people in the whole world will be generated by solar cells in the deserts. The world total energy consumption in 2007, that is, $5.1022 \times 10^{20}$ J can be generated in the form of electricity by solar cells with 15 % energy conversion in only 2.00 % of the main deserts on Earth, if 1000 Wm$^{-2}$ of solar energy are available for 8 hours a day. The intermittent and fluctuating electricity will be used for production of hydrogen by seawater electrolysis at nearby desert coasts. Because there are no infrastructures for mass transportation and combustion of hydrogen, hydrogen will be converted to methane, that is, the main component of natural gas, by the reaction with carbon dioxide at the desert coasts. After combustion of methane carbon dioxide will be captured and transported back to the desert coasts. Among systems in global carbon dioxide recycling, seawater electrolysis and methane formation by the reaction of carbon dioxide with hydrogen have not been performed industrially.

We created anodes for oxygen evolution without chlorine formation in seawater electrolysis, energy-saving cathodes for hydrogen production and ideal catalysts for methane formation by the reaction of carbon dioxide with hydrogen. We constructed a prototype plant for global carbon dioxide recycling in 1995 and an industrial scale pilot plant consisting of seawater electrolysis and carbon dioxide methanation in 2003.

The current status of creation of key materials, systems and plants will be shown. We are now concentrating our efforts to decease the price of methane by improving the key materials and systems.


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**CO₂ Capture from ambient air**

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An amine-modified solid sorbent was developed for CO₂ capture directly from ambient air. CO₂ adsorption is carried out at 25°C and atmospheric pressure from an air stream with 430 ppm CO₂ concentration and 40% relative humidity, while pure CO₂ is driven off the sorbent upon heating to 95°C. The sorbent showed to be fully recyclable during cyclic CO₂ adsorption-desorption experimental runs.

Most CO₂ capture technologies deal with the scrubbing of CO₂ from flue gases [1], although stabilization of global CO₂ emissions is unlikely to be achieved without CO₂ capture from atmospheric air [2,3]. The minimum amount of energy required for gas separation, given by the Gibbs free energy change of the process, is 5.2kJ/mol for 12% CO₂ concentration in flue gases, and 18.9kJ/mol (4 times more energy) for 430 ppm CO₂ concentration in air (280 times more diluted). However, the capture of CO₂ from air can be performed conveniently at locations with high solar energy resources and coupled to its recycling for the production of solar liquid fuels [3]. Previous studies considered adsorbers based on calcium [4], sodium [5,6], amines [7], and ion-exchange resins [8,9,10].

Herein, an amine-modified solid sorbent was studied as CO₂ capture structure. Experiments were performed for CO₂ adsorption at 25°C and atmospheric pressure using an air stream with 430 ppm CO₂ concentration and 40% relative humidity, followed by pure CO₂ desorption upon heating to 95°C. The sorbent showed to be fully recyclable during consecutive CO₂ adsorption-desorption cyclic runs. We describe in detail the experimental setup and results.

Acknowledgement - This work is being partially financed by the GEBERT-RÜF-STIFTUNG.

**References**

[1] Intergovernmental Panel on Climate Change (IPCC), Fourth Assessment Report
Sunfire: 3rd generation Fuels from CO₂ and h₂O

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3rd generation fuels produced from CO₂ and H₂O by coupling in renewable energy can provide preferable energy density, transportation and storage characteristics due to their liquid state. However, at state of the art, energetic efficiency of fuel synthesis from CO₂ and H₂O is at ~50% (electric energy/fuel energy), significantly lower than the production of pure hydrogen.[2] SunFire has established a technological process that can achieve efficiencies above 70%.[1][3] A study has been conducted to evaluate the total value chain of such a “closed carbon cycle” and to identify commercial potentials.

Synthesis of fuels from CO₂ & H₂O

For the production of fuels (-CH₂-) from CO₂ and H₂O, both educts need to be reduced. The required energy can be coupled in electrically, thermally or from solar light.[1] However, such processes usually start with the production of pure Hydrogen which is used for reducing CO₂ to CO. In a second step, CO and H₂ are mixed to syngas and converted into -CH₂- and H₂O. This implies the need of three molecules H₂ for one compound of -CH₂-. Considering the difference between HHV and LHV for H₂O and the heat losses of the exothermic synthesis, such a process can practically not exceed an energy efficiency of ~50% without sophisticated recuperation.[2] SunFire has developed a technological process that utilizes electrolysis to produce Hydrogen, Reverse-Watergas-Shift-Reaction to reduce CO₂ to CO and finally syntheses -CH₂- via Fischer-Tropsch. The process can reach efficiencies of ~70% to turn electric energy into chemical enthalpy of liquid fuels.[1][3]

Value and supply chain

The value chain of a “closed carbon cycle” has been examined in a study with industrial and scientific partners. It starts with H₂O- and CO₂-capture, considers the conversion into fuels and takes into account all required logistics for transport and fuel distribution. As a result, the energetic efficiency of the total supply chain (Well-to-Tank) is estimated to be ~60%. The cost for 3rd generation fuels shall be around 1,2 €/litre Diesel.[3]

References

[3] The SunFire-study is under non-disclosure but significant details shall be presented in the symposium.

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Formic acid – The key compound in a viable hydrogen storage system

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Hydrogen can be generated very efficiently from formic acid in aqueous phase homogeneous catalytic reactions, using ruthenium catalysts with water-soluble phosphate ligands. Although this reaction results only two gas products, heterogeneous catalysts could be advantageous for recycling, especially for dilute formic acid solutions, or for mobile, portable applications. On the other hand, the straightforward reduction of CO$_2$ leads to the production of formic acid, making this system suitable for hydrogen storage.

Introduction
Carbon dioxide is the primary carbon source in the atmosphere. One promising approach for the introduction of CO$_2$ as C$_1$-source in synthetic chemistry is its catalytic hydrogenation to form formic acid or its salts or adducts.

Experimental
The homogeneous catalytic decomposition of formic acid and the carbon dioxide hydrogenation reactions have been carried out under mild experimental conditions in aqueous solutions.

Results and discussion
The water-soluble sulfonato aryl- and aryl-/alkylphosphine ligands have been applied successfully in aqueous-phase ruthenium(II)-catalyzed formic acid decomposition into hydrogen and carbon dioxide [1]. Active catalysts for the benign hydrogenation of carbon dioxide and bicarbonate in water are intensively investigated [2].

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References


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Surface Oxidation of Hydrides

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Surface properties of various hydrides, i.e. covalent-like hydride (AlH₃), complex metal hydride (Mg₂NiH₄), and complex hydride (LiBH₄) including the composite system (2NaBH₄ + MgH₂) were investigated. The surface processes on the hydrides are discussed with respect to the hydrogen desorption kinetics, surface oxidation, and catalyst preparation.

Effect of surface oxidation

The surface condition, i.e. surface composition and oxidation state of hydrogen storage material is crucial to the hydrogen sorption processes [1].

\[ \text{suppression of diborane formation by the oxides, e.g. Li₂O, on the surface (schematic)} \]

Catalyst for hydrogenation of CO₂

The hydride Mg₂NiH₄ was modified by oxidation and combining hydrogen absorption/desorption circles. The prepared catalyst yields 100% CO₂ conversion and 100% selectivity to CH₄ in the reaction, \( \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \) at 580 K.

References


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LiBH$_4$ and Ti-Catalyzed Nanocrystalline MgH$_2$ Composite for Hydrogen Storage

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Using Ti-catalyzed MgH$_2$ nanocrystalline material, a 2LiBH$_4$+nano MgH$_2$ composite sample shows significantly enhanced kinetics and different thermodynamics performances compared to a 2LiBH$_4$+commercial MgH$_2$ composite. Its desorption temperatures are 50-70°C lower compared to 2LiBH$_4$+commercial MgH$_2$ composite sample when desorbed to evacuated space.

![Fig.1 PCI curves of 2LiBH$_4$+nano MgH$_2$ composite at different temperatures.]

The reaction pathways during desorption of this composite between 304-383°C were studied. It is the first time that three obvious plateaus are found during the PCI desorption process of this kind of composites. During the PCI desorption of 2LiBH$_4$+nano MgH$_2$ composite, three obvious plateaus are observed between 357~383°C. The desorption reactions for these three plateaus are MgH$_2$ $\rightarrow$ Mg + H$_2$, Mg + 2LiBH$_4$ $\rightarrow$ MgB$_2$ + 2LiH + 3H$_2$ and 2LiBH$_4$ $\rightarrow$ 2B + 2LiH + 3H$_2$, respectively. The reaction Mg + B $\rightarrow$ MgB$_2$ takes place after the last reaction at temperatures between 357 to 383°C. At 304 and 335°C, two plateaus are found during the PCI desorption of the 2LiBH$_4$+nano MgH$_2$ composite, corresponding to MgH$_2$ $\rightarrow$ Mg + H$_2$ and 2LiBH$_4$ $\rightarrow$ 2B + 2LiH + 3H$_2$.

References


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New Catalyst for Hydrogen Evolution and Oxygen Reduction

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A dream device for hydrogen production by water splitting will be discussed. Here we have investigated new electro-catalysts that — combined with semiconductors that can harvest the red part of the solar spectrum — could replace expensive and scarce materials such as Platinum metals. Various Molybdenum sulfides and Tungsten sulfides mimicking nature’s enzymes for hydrogen evolution will be discussed [1-4]. The optimal configuration for hydrogen evolution and electron-hole separation will also be demonstrated as shown in Figure 1 where an incomplete $\text{Mo}_3\text{S}_4$ Cubane is used for evolving hydrogen.

Figure 1 shows the principle of a dream device harvesting the solar light and separating the oxygen and hydrogen evolution in a tandem device. The blowup shows Cubanes deposited on Si-pillars catalyzing the hydrogen evolution by help of the red part of the solar spectrum.

Utilizing the hydrogen can be done in a Proton Exchange Membrane Fuel Cell and here the most pronounced losses are related to the oxygen reduction reaction on the cathode side. New electro-catalysts for the Oxygen Reduction Reaction (ORR) will also be discussed with particular focus on alloy catalyst of Pt and early transition metals [5].

References


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Ib Chorkendorff
High temperature Steam and Steam / CO₂ Electrolysis Research and Development at the INL

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The Idaho National Laboratory (INL) has been studying the feasibility of using solid oxide fuel cells (SOFCs) as electrolyzers for large-scale, high temperature (efficient) nuclear-powered hydrogen production, as well as various other deployment schemes, including coelectrolysis of steam and CO₂ for syngas production. INL’s research and development program includes experimental testing at various scales, computational fluid dynamics modelling, and process systems analysis. Overall, the use of SOFCs for hydrogen production appears promising once issues concerning cell durability are solved.

Background

World production of H₂ is currently about 42 million tons per year: 48% from natural gas, 30% from oil, 18% from coal, and 4% from electrolysis [1]. In other words, 96% of the world’s hydrogen is produced from fossil fuels. When fossil fuels are used for hydrogen production, significant quantities of the greenhouse gas CO₂ are produced as a byproduct. Obviously this is not a sustainable means of satisfying H₂ demand for the future.

The Idaho National Laboratory (INL) has been assessing the feasibility of using SOFC technology for high temperature electrolysis of steam for large scale sustainable hydrogen production. In parallel, the INL is studying the simultaneous electrolysis of steam and carbon dioxide for syngas production. When linked to a nuclear power source, this technology provides a carbon neutral means of producing hydrogen via water splitting or producing syngas / synfuels from water and CO₂. High temperature electrolysis has an additional advantage of essentially instantaneous “load following” capability, as well as fast startup and shutdown times (ramping). The load following capability of high temperature electrolysis makes it also an attractive match for renewable (intermittent) energy sources (wind, solar, etc.) as well.

INL Program

Although high temperature electrolysis leverages SOFC technology, the concept is still not ready for commercialization. There are fundamental differences in the two modes of operation such that performance cell performance degrades faster in the electrolysis mode of operation. This issue has been identified as the major barrier to technology development. The INL has been studying and testing various cell designs and materials from various manufacturers as well as performing specialized modeling to understand what phenomena are the primary contributors to cell performance degradation. INL investigations have included button cell tests, single cell tests, multi-cell stacks, multi-stack system tests, as well as computational fluid dynamics and systems-level simulations.

References


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Hydrogen Production from Water

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Homogenous photocatalytic water reduction systems known today are often limited both by the stability of the participating catalysts in terms of turnover numbers and by their activity in pure aqueous solutions. Profound knowledge of the mechanism allowed the systematic design of derivatized catalysts to improve the stability and activity of such a system in water.

Photocatalytic water reduction

A system employing rhenium photosensitizers, cobalt complexes and sacrificial electron donors was used to produce hydrogen with visible light from aqueous or organic media (Scheme 1).[1] A detailed analysis of the hydrogen release allowed to identify the cobalt species as the stability and rate limiting factor.

Scheme 1. Proposed photocatalytic cycle

Cobalt macrocyclic complexes are known to produce hydrogen under reducing conditions upon addition of protons.[2,3] However, in the present system the turnover numbers are very limited (<150), most probably due to an intramolecular metal to ligand hydride shift at the cobalt centre. By introducing electron donating or accepting ligands, the reactivity of this hydride could be tuned to increase the rate of hydrogen release or to slow down the rate of the hydride shift, respectively. Hydride formation and possible heterolytic hydrogen release from such hydrides are obviously pH dependent. Variation of the pH therefore plays an important role in the understanding of the mechanism. Detailed mechanistic analysis of the catalytic cycle as a function of solvent, pH and synthetic derivatisation of the catalysts will be presented.

References


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Competitive Chlorine and Oxygen Evolution from Sea Water at Rutile (110) Surfaces, from First Principle Calculations


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Introduction

It is well known that out of all water on Earth only 2.75 percent is fresh water including 2.05 frozen in glaciers and that the rest of 97.25 is represented by waters having different degrees of salinity. Electrochemical water splitting or oxygen evolution reaction (OER) has attracted great interest in the recent years as a key process in hydrogen production from sunlight [1]. Thereby, this process will be performed mostly from waters with different concentrations of chloride anions. Despite the fact that the equilibrium standard potential for Cl₂ evolution (1.36 V) is higher than that of oxygen evolution (1.23 V), it is well known that chlorine evolution (ClER) is a competitive reaction to that of oxygen evolution reaction (OER) on the most active surfaces that perform well for OER [2-3]. Accordingly understanding this process is crucial in order to design catalysts selective only for oxygen evolution.

Results

Starting from first principle calculation, we will show the reason why ClER is preferred instead OER, on the most active surfaces for OER and which are rutile oxides: IrO₂, RuO₂, PtO₂, MnO₂ etc. We show that linear correlations between Cl and O adsorption energies exist, so the catalysts that are good for oxygen evolution are also good for chlorine evolution. Using these relations a generalized phase diagram was drawn across a potential range, where binding energy of oxygen is a descriptor. ClO² and Cl(O)₂ will form spontaneously on the cus sites of IrO₂ and RuO₂ at the potential required for chlorine evolution. Based on the reaction free energies of intermediates, an electrochemical analogue to Sabatier analysis is derived for chlorine evolution and for oxygen evolution and we show that RuO₂ is on top of the volcanoes followed by PtO₂ and IrO₂. On all studied surfaces the potential for chlorine evolution is smaller than the potential for oxygen evolution, and thereby indicating why Cl₂ is the main product which is produced during electrochemical water splitting.

References


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Oxygen Evolution Reaction on Single Crystalline Electrodes

Chinmoy Ranjan

Clean hydrogen obtained from water using electrochemical water splitting. Splitting involves two steps: oxidation of water molecule to form oxygen (anodic reaction) and protons and then reduction of protons (cathodic reaction) to obtain hydrogen. The cathodic reaction is very facile and easily happens at various catalysts whereas the anodic oxygen evolution reaction is kinetically difficult and currently uses a huge over potential (to overcome the kinetic barrier) even on state of the art catalysts.

Solution to this problem is essential towards the successful implementation of a hydrogen based energy economy.

We investigated electrochemical behavior of single crystalline surfaces of noble metals probing into surface oxidation and surface modification with occurring with oxygen evolution reaction and carry out surface science experiments to understand the nature of oxygen evolving catalysts.

We present our results on comparative studies on Pt single crystalline electrodes. We find differences in kinetic behaviours of various surface terminations indicating a dissimilar mechanism of oxygen evolution reaction on these surfaces.

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Electrochemical Investigation of Advanced Materials Used for Development of Alkaline Electrolyzer’s Diaphragms

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The alkaline electrolyzers industry is facing the imminent necessity to replace the traditionally used asbestos diaphragm, with a separator made of advanced environmentally friendly materials. The advanced material should fulfill multiple requirements, such as: good gas separation and fast evacuation of the bubbles from the surface, increased ionic conductivity and low cell overpotential, chemical stability in 25 wt. % KOH solution at 85°C. Also, the material should possess the mechanical strength, be cost effective and ecologically accepted. The investigation of the effect of porosity on the ionic conductivity of zirconium dioxide, which represents the basic compound for the development of ceramic diaphragms, is undertaken.

Material development

Zirconium dioxide represents the basic compound for the development of ceramic diaphragms. The investigation of the influence of different porosity on the ionic resistance of zirconium dioxide based diaphragms has been undertaken. By varying the content of carbon as a pore former (0, 20 and 40 vol. % C) during the process of diaphragms sintering at the pressure of 36 MPa and the temperature of 1200 °C, different porosity is obtained.

Ionic resistivity

Ionic conductivity of developed materials was determined by electrochemical impedance spectroscopy (EIS). Two compartment, four electrodes electrochemical cell served for EIS measurements using Zahner potentiostat. Measurements were performed in 25 wt. % KOH solution at ambient temperature, by sweeping frequencies from 1 MHz to 10 mHz in potentiostatic mode. Different techniques, such as gas adsorption (BET), mercury intrusion porosimetry (MIP), and scanning electron microscopy (SEM) served for micro-structural characterization (porosity determination) of developed diaphragms.

EIS spectra showed the purely resistive behaviour of investigated diaphragms. Diaphragms conductivity as a result of these measurements was correlated to the materials porosity and tortuosity.

References


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Hydrogen Adsorption in Advanced Carbon Materials

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Due to the fact that the physisorption energy of hydrogen on carbonaceous materials is low and on the other hand the chemical binding energy of hydrogen is too high, different approaches are attempted to increase the physisorption energy to usable values (30-40 kJ/mol H₂). For the hydrogen adsorption on carbonaceous materials it is known that the gravimetric hydrogen density is proportional to the specific surface BET area of the material. 1.5 mass% per 1000 m²/g were determined electrochemically at room temperature [1]. The hydrogen adsorption on different materials like a-C, graphene, Li₅C₆₀ and Mg₅C₆₀ and was investigated.

Introduction

The hydrogen binding energy increases on curved carbon sheets due to the rehybridization from sp² to sp³ of the carbon network [3, 4]. The binding energy can further be increased by charging the surface e.g. charged C₆₀ [5]. An interaction between H₂ and metal ions is also established by electro-static or orbital interaction (Kubas [6]).

Experimental

Graphene was produced via exfoliation of graphite oxide or by solvothermal synthesis. The M₅C₆₀ was synthesized by mixing C₆₀ powder directly with the metal and subsequent heat treatment [7]. The hydrogen adsorption in a-C, graphene, Li₅C₆₀ and Mg₅C₆₀ was investigated volumetrically. Depending on the material, the hydrogen adsorption was investigated between 77 and 873 K and hydrogen pressures up to 100 bar. The BET surface area of the material was determined and compared with the hydrogen uptake.

References


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Hydrogen interaction with graphene probed by µSR

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The interaction of hydrogen with defective graphene produced via chemical methods is investigated by muon spin relaxation spectroscopy. In-plane defects could dissociate the hydrogen molecule and absorb up to two hydrogen atoms at the same site. An unexpected mobility of the hydrogen atoms absorbed onto the graphene surface is inferred by the experimental data.

Hydrogen in graphene
The recent Nobel prized discovery of graphene has renewed the interest towards carbon based materials for hydrogen storage applications. Thanks to the huge specific surface, the light weight and the exceptional mechanical properties, optimised graphene-based systems are expected to bear good reversibility, fast kinetics and high capacity, as suggested by the studies on metal decorated nanostructures and GOFs [1,2].

Synthesis
Gram quantities of graphenes are obtained from the thermal reduction of graphite oxide (GO). GO is produced with Brodie method (oxidation of graphite with fuming HNO₃ and KClO₃). Hydroxyl, epoxide and carboxyl groups attached on the graphene sheets are then removed by thermal shock at 1320 K in vacuum and their desorption allows to separate the single graphene layers. An intermediate partial reduction with NaBH₄ allows to control the amount of in-plane defects in the graphene sheets. Graphene samples may then be treated in H₂ (or D₂) flux at different temperatures (from 973 to 1273 K) and thoroughly characterised.

µSR on graphene
Both in-plane defects (vacancies) and edges in graphene sheets are known to promote the dissociative absorption of molecular hydrogen (dissociation barrier of 1.1 eV [3]) and to easily absorb atomic hydrogen. We investigated the samples with Muon Spin Relaxation Spectroscopy (µSR), technique which consists in implanting muons (chemically analogous to light hydrogen nuclei) in the sample and following their spin evolution. Data show that up to 30% of implanted muons experience the dipolar field of a µ-H entangled state with d_µ-H = 1.75Å, suggesting that up to two hydrogen atoms could saturate an in-plane carbon vacancy in a stable configuration. Moreover, the unexpectedly high capture cross-section, if compared with the estimated number of defects in the graphene planes (of the order of 100 ppm), suggests that muons (and hence also hydrogen atoms) could easily diffuse onto the graphene plane before being trapped by the defects.

References

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Neutron total Diffraction for structural studies of hydrogen storage materials

Toshiya Otomo
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New neutron total diffractometer, NOVA, was constructed at J-PARC (Japan Proton Accelerator Complex) for structural analysis of hydrogen storage materials. NOVA observes powder diffraction and small-angle scattering simultaneously. It is at the final commissioning phase and recent results obtained by NOVA show its usefulness for hydrogen materials study.

Neutron total diffractometer, NOVA

Neutron diffraction technique is a powerful probe to observe and analyze hydrogen position in materials. “Total scattering” is a technique that had been developed for disordered materials studies and is now widely used to observe non-crystalline features in materials. The word, “total”, came from obtaining real-space pair correlation function, which contains every atomic correlation, by Fourier transforming measured diffraction pattern. A neutron total diffractometer, NOVA, was constructed at J-PARC to observe hydrogen storage materials.

Study of hydrogen storage materials by NOVA

By adapting neutron total scattering to hydrogen storage materials, variety of structural information such as hydrogen-hydrogen correlation even in disordered phase can be analyzed. One of the most prominent features of NOVA is the ability to analyze structures of amorphous and liquids structure as well as crystalline structure. To observe hydrogenation and dehydrogenation process, in-situ sample environments such as H$_2$/D$_2$ gas atmosphere (up to 10 MPa, 50 K ~ 473 K) and high-temperature (up to 1373 K) have been equipped on NOVA. As a total diffractometer, NOVA covers a wide momentum transfer range, 0.01 Å$^{-1} < Q < 100$ Å$^{-1}$ in one measurement. This wide-Q measurement ability is also useful for meso-structure and nearest atomic correlation simultaneously. Based on the high neutron flux of J-PARC, real-time observation of non-equilibrium state is feasible.

During the commissioning of NOVA, several samples were measured to confirm instrument performance. Some of recent results including VD$_{1.8}$, AlD$_3$ and LiAl(NH$_2$)$_4$ will be presented.

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Born 5. 9. 1965 in Japan. 1993 Dr. of Engineering from Tohoku University and Post Doctoral fellow at Institute for Material Research, Tohoku Univ. 1994 Research associate, High Energy Physics Laboratory (former name of High Energy Accelerator Research organization, KEK). 2003 Associate Professor, KEK. 2008 Professor, KEK. 2009 Guest Professor at IMR, Tohoku University in Sendai, Japan. Guest Professor at Kyushu University in Fukuoka, Japan. 2009- Member of the council of Japanese Neutron Scattering Society.

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What can we learn from EXAF’s for hydrogen storage materials?

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Extended x-ray absorption fine structure (EXAFS) is an element specific method to provide information about the local structure, such as the nature and number of surrounding atoms around an absorber atoms and their interatomic distances. Here, we show the strengths of EXAFS for hydrogen storage research for two show cases i.e., nano sized Mg-Ni supported on carbon scaffold \cite{1} and Ti-doped Mg\textsubscript{2}Ni thin film systems \cite{2}. EXAFS was applied to characterize the local structure of Ni upon hydrogen cycling.

The Mg-Ni carbon systems \cite{1} were prepared by melt infiltration of MgH\textsubscript{2} under H\textsubscript{2} pressure into the nano pores of a carbon scaffold. On/in this carbon first 12 wt\% Ni was deposited. TEM results show that the size of Mg-Ni particles is only a few nanometers thus too small to be visualized by XRD. Ni K-edge EXAFS was measured upon hydrogen cycling. For the hydrogenated state, Mg\textsubscript{2}NiH\textsubscript{4} and very small Ni particles (CN = 2.9) were detected. After dehydrogenation, the phases were deduced to be agglomerated Ni particles with a CN of 8.2 together with Mg\textsubscript{2}Ni particles (CN Ni-Mg = 3.9). After rehydrogenation the Ni-Ni coordination number decreased again to 2.1. This structural reversibility parallels that of the hydrogen storage reversibility.

For the Ti-doped Mg\textsubscript{2}Ni thin film system \cite{2}, hydrogenography shows that the hydride formation enthalpy of Mg-Ni is drastically altered upon Ti doping. Also, density functional theory (DFT) calculation results indicate that the destabilization mechanism of Mg-Ni-H system by Ti doping is due to the formation of Mg\textsubscript{2}Ni and Ti-Ni intermetallics in the as-deposited state, which transform into a metastable Ti-doped Mg\textsubscript{2}NiH\textsubscript{4} phase upon hydrogenation \cite{3}.

Our Ni K-edge EXAFS results show that for the as prepared state of Mg-Ni-Ti, the phases are indeed Mg\textsubscript{2}Ni and Ti-Ni intermetallics. After hydrogenation, we deduce the presence of a Ti-doped Mg\textsubscript{2}NiH\textsubscript{4} in which Ti substitutes the Mg positions. The model for the Ti-doped Mg\textsubscript{2}NiH\textsubscript{4} matches very well with the experimental data.

References


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Mg-based optical Hydrogen sensors

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The equilibrium pressure of the hydride formation of Pd-capped Mg thin films can be tuned by varying the Mg thickness. This remarkable property combined to the large optical change upon hydrogen absorption (switchable mirror effect) can be exploited in order to make a Mg-based optical sensor able to measure a continuous range of hydrogen partial pressures. Such a device works also in reflectance, providing a direct reading by human eye.

Optical hydrogen sensor

The development of hydrogen based energy systems drives the research for reliable safe and cheap hydrogen sensors. Conventional hydrogen sensors make use of electrical leads which may induce sparks and provide a cause for ignition. Optical sensors operate safely in hazardous atmospheres thanks to the possibility of separating the optical read-out from the sensing area. The fiber optics hydrogen detector represents a unique combination of small dimensions, low cost, and safe operation but it only indicates whether the hydrogen pressure overcomes the threshold level, set by the nature of the metal hydride sensing layer \cite{2}. We designed a sensor which exploits the thickness dependence of the equilibrium pressure of Pd-capped Mg thin films. The device basically consists of a sensing Mg layer with a thickness gradient along the longitudinal direction. Such a device shows a one-to-one relationship between the lateral progression of a visible optical change along the Mg gradient and the $H_2$ partial pressure varying in the range between 200 and 4000 Pa. The optical change of the Mg layer during the metal-hydride transition can also be detected in reflection, thereby allowing for multifiber applications.

References


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SCIENCE OF HYDROGEN & ENERGY AWARD

The “Science of Hydrogen & Energy” award is a price, 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.
SCIENCE OF HYDROGEN & ENERGY AWARD 2007

Ronald Pierre Griessen, was born March 7, 1945 in Switzerland. He received 1964 his Baccalauréat, from Gymnase français in Bienne, Switzerland. From 1964 – 1969 he studied Physics and Mathematics at the Swiss Federal Institute of Technology (ETH) in Zürich and finished with a Diploma-thesis on: "Magnetostriction of type-II superconductors". From 1969 – 1973 he was PhD student in the Low Temperature Physics Group of Prof.dr J.L. Olsen at the ETH. PhD-thesis on: "Oscillatory Magnetostriction and the stress dependence of the Fermi Surface of Al, In, Zn and Mg". From 1974 – 1976 he was Research Associate at the McLennan Physical Laboratory of the University of Toronto, Canada where he worked on the electronic structure of spin-density-wave systems and quantum oscillations. In 1976 he was visiting scientist at the ETH, Zürich and from 1976 – 1980 senior lecturer at the Vrije Universiteit in Amsterdam. Since 1980 he is Full Professor in charge of the Department of Condensed Matter Physics.

Ronald Griessen has investigated the thermodynamics of palladium films and the isotope effect on the electronic structure of hydrides. Furthermore, the effect of anharmonicity and Debye-Waller factor on superconductivity of PdH\textsubscript{x} and PdD\textsubscript{x} have been studied by Ronald before he developed a semi-empirical model for the heat of solution of hydrogen in transition metals. He also studied the trapping energy for hydrogen on lattice defects as well as the heat of solution of disordered transition metals. The volume expansion upon hydrogen absorption, the Gorsky-effect, the diffusion, electromigration and the hydrogen diffusion in magnetig fields are just a few other subjects treated and described by Ronald Griessen. Then Ronald decided to test the world of high pressure hydrogen and described the properties of hydrides formed at very high pressure as well as the properties of hydrogen gas in a wide temperature and pressure range. During the intense investigation of superconductors and metal hydrides under high hydrogen pressure in a diamond anvil cell, Ronald has discovered the switchable optical properties of yttrium and lanthanum hydride films. This has then stimulated Ronald to investigate thin films with optical methods and to develop new methods for the combinatorial search of new hydride phases as well as for the determination of the thermodynamic parameters e.g., stability and kinetics of the hydrides. Furthermore, new applications for hydrides as hydrogen detectors and optical filters have been developed in his group.
Louis Schlapbach, born March 4, 1944 in Belp, Switzerland. He graduated from the Swiss Federal Institute of Technology Zurich (ETHZ) in Experimental Physics and got his PhD in Solid State Physics – Magnetism also at ETHZ. As a postdoc at a CNRS laboratory in Paris, he studied hydrogen storage in intermetallic compounds. Back at ETHZ, he developed the surface science aspects of the hydrogen interaction with metals and alloys. From 1988 till 2001, Louis Schlapbach was Full Professor for Physics at the University of Fribourg. As such he built up a research team of 20-25 people working on the topic „New Materials and their Surfaces“ resulting in about 40 PhD, 200 scientific papers and some patents. A strong collaboration with industry was established. In spring 2001, he has been appointed CEO of Empa, the materials science and technology institution of the ETH domain with 750 coworkers in Dübendorf, St. Gallen and Thun.

Louis Schlapbach started his scientific work in 1970, 38 years ago, with the investigation of the Hall effect, electrical transport and magnetic susceptibility of liquid rear earth elements like Cerium. 30 years ago in 1970 he was coauthor with Busch and Waldirich on a paper about the hydrides of La-Ni compounds. LaNi$_5$ was subsequently investigated in view of the structure, surface segregations, hydrogen occupation of interstitial sites and as electrode material. LaNi$_5$ is still the base material for most of the electrochemical applications of metal hydrides today. The work on LaNi$_5$ was complemented by the research on FeTi. Louis Schlapbach 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 LaNi$_5$ 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 Schlapbach 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 Schlapbach edited the two books "Hydrogen in Intermetallic Compounds I & II" of the Springer Sereies. The books became a very important reference for all the researchers active in the field of hydrides.
SCIENCE OF HYDROGEN & ENERGY AWARD 2009

Gary Sandrock received his master from the Institute of Technology, Cleveland in 1965 and his Ph.D. from the Western Reserve University, Cleveland in 1971. He worked from 1962-1969 as a research metallurgist in the NASA Lewis Research Center, Cleveland, Ohio. From 1971-1983 he was Section Manager of Energy Systems at Inco Research and Development Center, Suffern, NY. From 1983-1991 he was Vice President and Director of Technology at Ergenics, Inc., Ringwood, NJ. From 1992-1993 Gary Sandrock was visiting professor at the Kogakuin University, Hachioji, Tokyo, Japan where he developed a new chemical surface treatment and investigated the activation characteristics of chemical treated $\text{AB}_n$ alloys. Gary then became the president of SunaTech, Inc., Ringwood, NJ, where he developed reversible hydrogen storage systems. At the same time Gary Operating Agent, International Energy Agency Hydrogen Implementing agreement Tasks 12 & 17 (Hydrogen Storage Materials) and worked as a consultant for the US DOE via Sandia National Laboratories, Livermore, CA.

In 1995 Gary Sandrock started to creat and maintain Hydride Databases of IEA(HIA)/DOE/SNL (http://hydpark.ca.sandia.gov) and he is author of several book chapters and review papers e.g. “A panoramic overview of hydrogen storage alloys from a gas reaction point of view”. His recent research concentrates on the catalysis of the hydrogen desorption from alanates and most recently Gary investigated the hydrogen desorption behavior of AlH$_3$ and explained the mechanism of the kinetic stabilisation of aluminumhydrid. Furthermore, he published a paper entitled “Accelerated thermal decomposition of AlH$_3$ for hydrogen-fueled vehicles” where he shows the possible ways to change the activation barrier for the hydrogen desorption in a controlled way.

Gary Sandrock not only made significant achevements in understanding metal hydrides he also built the bridge from sciences to application. Furthermore, his scientific review papers and the hydride database are inestimably value for the hydride society.
Jens Norskov was born on September 21 in 1952. He received his Master degree in physics and chemistry from the University of Aarhus, Denmark in 1976 and his PhD in theoretical physics in 1979. During his PhD he published papers about the electronic structure of H and He in metal vacancies and the contraction of diatomic molecules upon chemisorption. Jens Norskov was a Post Doc at IBM in Yorktown Heights, New York in 1979 and was affiliated with Nordita, (Nordic Institute for Theoretical Physics) in Copenhagen before he became a member of the scientific staff of Haldor Topsøe A/S, Lyngby in 1981. He continued the investigation of gas molecules at the surface of metals and developed a picture of adsorption and desorption of hydrogen emerging from self-consistent model calculations. In 1992 he was appointed as a professor of theoretical physics in the department of physics at the Technical University of Denmark, Lyngby and became the director of the Center for Atomic-scale Materials Physics (CAMP), Department of Physics, Technical University of Denmark, Lyngby.

Recent research of the group of Jens Norskov covers several of the most relevant topics: 1) The development of theoretical methods e.g. “Scaling Properties of Adsorption Energies for Hydrogen-Containing Molecules on Transition-Metal Surfaces”; 2) Theoretical surface science e.g. “Role of strain and ligand effects in the modification of the electronic and chemical properties of bimetallic surfaces”; 3) Nanostructures and materials properties e.g. Atomic-scale imaging of carbon nanofiber growth”; 4) Heterogeneous catalysis e.g. “Ammonia synthesis from first principles calculations”; 5) Biomolecules e.g. “Biomimetic hydrogen evolution”; 6) Electrochemistry and fuel cells e.g. “The origin of the overpotential for oxygen reduction at a fuel cell cathode”; 7) Hydrogen storage e.g. “Metal ammine complexes for hydrogen storage”

Jens Norskov is not only a creative and brilliant scientist, he also belongs to the few scientist able to successfully combine theoretical approaches with experimental observations for the understanding of the basic phenomena. It is always a great pleasure to listen to Jens Norskov’s talks, which are exciting eye opening stories combined with some great new stimulating ideas.
SCIENCE OF HYDROGEN & ENERGY AWARD 2010

Prof. Dr. Rüdiger Bormann was born September, 14 1952 in Germany. He received 1977 his diploma in physics (Metalphysics), from the University Göttingen and 1979 his Dr. rer. nat. from the University Göttingen. From 1981 to 1982 he was visiting scientist in the Dept. of Applied Physics at Stanford University, U.S.A. From 1982 to 1988 he was Assistant Professor (Hochschulassistent) at the University Göttingen where he received the Habilitation University Göttingen, venia legendi in 1988. From 1989 to 1997 he was Professor of Metalphysics (GKSS Research Centre, Geesthacht and Hamburg University of Technology) and from 1996 to 2009 he was director of the Institute for Materials Research, GKSS Research Centre, Geesthacht and since 2009 he is Professor of Applied Materials Physics and President of the University of Bayreuth.

Prof. Rüdiger Bormann investigated 20 years ago the free energy of metallic glasses, metastable crystalline and amorphous alloys as well as the thermodynamics and kinetics of the amorphous phase formation by mechanical alloying. This was the basis for the investigation of Mg and Mg-Ni hydrides and the thermodynamics of nanoscale magnesium hydride. The discovery catalytic effect of metal oxides on the hydrogen sorption kinetics of magnesium was a great step forward in the development of hydrogen storage materials. Furthermore, very important was also the interpretation of the role of the grain boundaries for the diffusion of hydrogen in the passivating hydride phase formation. Recently the discovery of the so called reactive hydride composites by the combination of two hydrides has opened a new field of materials design for hydrogen storage. Therefore, we award Prof. Rüdiger Bormann with the Science of Hydrogen & Energy prize 2010.
SCIENCE OF HYDROGEN & ENERGY AWARD 2010

Ivor Rex Harris was born August 31, 1939 in United Kingdom. In 1960 he received his B.Sc. in Physical Metallurgy from the University of Birmingham, 1964 his Ph.D and became a ICI Research Fellow. From 1966 he was lecturer in the Department of Physical Metallurgy and in 1988 he became a full Professor of Materials Science. From 1989 to 2002 he was Head of School, Metallurgy and Materials and from 2004 to 2005 acting director of the Institute for Energy Research and Policy. Since 2008 he is Honorary Professor of Materials Science of the School of Metallurgy and Materials at the University of Birmingham.

Prof. Dr. Ivor Rex Harris

For around 40 years, Rex Harris was leader of the Applied Alloy Chemistry Group (AACG) in Metallurgy and Materials. During this time he maintained a long-standing research interest in the fields of rare earth alloys, permanent magnets and hydrogen purification and storage materials. He developed a close synergy between these fields with the development and application of the Hydrogen Decrepitation (HD) process to the manufacture of NdFeB magnets. The HD process resulted in up to a 25% saving in production cost and is now used world-wide in the fabrication of NdFeB sintered magnets. These materials are playing a vital role in the production of energy efficient electric drives, actuators and generators. The latest development within the group is the use of the HD process in the recycling of 2/17 and NdFeB magnets. His research also made a very significant contribution to the development and understanding of the Hydrogenation, Disproportionation, Desorption and Recombination (HDDR) process which enabled coercive powder and hence bonded magnets to be formed from bulk NdFeB alloys. He has published over 500 scientific papers and edited and co-edited a number of books. During these years he has successfully supervised around 120 postgraduate students, many of whom are still working in applied materials science and occupy senior positions in industry, government and academia throughout the world. Since stepping down as group leader and head of school he has focused his activities on the application of NdFeB magnets and hydrogen storage materials to practical demonstrators such as the Ross Barlow hybrid canal boat. This zero-carbon emission craft is serving to highlight the huge potential of magnets and hydrogen in the drive towards a sustainable transport system and he has given a large number of public lectures on this subject with the aim of raising public awareness of the dual threats of climate change and resource depletion. He continues to be very active in this campaign which he considers to be of paramount importance. Therefore, we award Prof. Rex Harris with the Science of Hydrogen & Energy prize 2010.
SCIENCE OF HYDROGEN & ENERGY AWARD 2010

Rainer Kirchheim was born May 24, 1943 in Halle/Saale, Germany. He studied Physics at the University of Stuttgart from 1966-1971 and received the diploma for the work “Electrochemical studies of oxygen solid solutions in high melting metals” at the Max-Planck-Institut für Metallforschung/University of Stuttgart. He received his Ph.D. for the thesis entitled “Thermo- and electrotransport of oxygen and nitrogen in Va metals “ from the University of Stuttgart, Max-Planck-Institut für Metallforschung in 1973. In 1988 he received the Habilitation “Measurements and modelling of hydrogen solubility and diffusivity in disordered metal lattices“ from the University of Stuttgart, Faculty of Chemistry Metallurgy. Since 1993 he is Full Professor (Gustav Tamman Chair) University of Göttingen Göttingen Germany and Director Georg-August-Universitaet Göttingen, Institut für Materialphysik Göttingen Germany.

Prof. Rainer Kirchheim has investigated 30 years ago oxygen in metals, especially diffusion, thermo-transport and thermo-power of oxygen in transition metals and alloys. In 1980 he started to study diffusion of hydrogen in dilute alloys of copper and niobium in palladium. He developed an electrochemical method for the measurement of the hydrogen diffusion in palladium and palladium alloys and performed fundamental studies on the diffusion mechanism of interstitial species. The interaction of hydrogen with dislocations in palladium and the interpretation with a model based on the Fermi-Dirac distribution are of great importance for the understanding of the interstitial site occupation of hydrogen in alloys and amorphous metals.

For the enormous contributions on the hydrogen dynamics and thermodynamics in metals as well as the hydrogen interaction with dislocations, grain boundaries and interfaces we award Prof. Rainer Kirchheim with the Science of Hydrogen & Energy prize 2010.
SCIENCE OF HYDROGEN & ENERGY AWARD 2011

Koji Hashimoto was born October 23, 1935 in Japan. He received the M. Sc. in Chemistry from the Faculty of Science of the Tohoku University, Sendai, Japan. In 1966 he received the Doctor degree in sciences from the Tohoku University and in the same year he became an associate professor in the Institute for Materials Research (IMR) of the Tohoku University. From 1967 to 1969 he was a Post Doctorate Fellow in the Division of Applied Chemistry of the National Research Council in Canada.

From 1987 to 1999 he was a Professor in the Institute for Materials Research (IMR) of the Tohoku University and from 1999 to 2006 he was Professor at the Tohoku Institute of Technology.

He is in the Editorial Board of "Corrosion Science", a Member of NACE International, the Electrochemical Society and the International Society of Electrochemistry. Member of Japan Society of Corrosion Engineering, the Japan Institute of Metals, the Surface Finishing Society of Japan, the Iron and Steel Institute of Japan, the Electrochemical Society of Japan, the Society of Chemical Engineers, Japan, the Chemical Society of Japan, and other scientific societies in Japan.

He received many awards among those also The Electrochemical Society Fellow Award in 1997 in recognition of contribution to the advancement of science and technology, for leadership in electrochemical and solid state science and technology and for active participation in the affairs of the Electrochemical Society, Inc.

We award Prof. Koji Hashimoto for his outstanding work on the production of hydrogen and the use of hydrogen for the reduction of CO$_2$ with the Science of Hydrogen & Energy prize 2011.
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Information
Map from Zürich (upper left corner) to Stoos (center bottom)

Map of the region Schwyz-Stoos
Travel to Stoos from Zürich airport:
Please go to the ticket counter in the airport and ask for a ticket to Stoos (roundtrip). Please also ask the person at the counter to print you the timetable for your connection e.g.:

So, 23.01.11
Zürich Flughafen ab 14:13 3 IC 726, InterCity BZ RZ
Zürich HB an 14:23 17
walk from track 17 to track 4
Zürich HB ab 14:35 4 IR 2345, InterRegio
Zug an 15:01 4
change to train on opposite side of platform
Zug ab 15:05 3 S2 21247, S-Bahn Linie 2
Schwyz an 15:33 2
the bus is parked in front of the station
Schwyz, Bahnhof ab 15:36 Bus 1, Richtung: Muotathal, Hölöch
Schwyz, Schlattli an 15:54
the bus stops in front of the cable car station, show your ticket at the counter
Schlattli SSSF ab 16:10 FUN 19, Standseilbahn
Stoos an 16:18
Dauer: 2:05

EMERGENCY TELEPHONE NUMBERS

POLICE 117
FIRE FIGHTERS 118
AMBULANCE 144
RESCUE HELICOPTER 1414

Corinne Gianola 076 398 9985
Andreas Züttel 079 215 4601
Hotel Stoos, Reception 041 817 44 44
### Fahrpläne

#### Standseilbahn Schwyz/Schlattli–Stoos

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12 Fr & Sa 17.12.2010—9.4.2011 nur Bergfahrt
13 Fr & Sa 17.12.2010—9.4.2011 nur Talfahrt


#### Luftseilbahn Morschach–Stoos

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#### Sesselbahnen Stoos–Fronalpstock

Betriebszeiten 1. Sektion Stoos–Mettlen: 8.30–16.30 Uhr
Betriebszeiten 2. Sektion Mettlen–Fronalpstock: 8.30–16.15 Uhr

#### Sesselbahn Klingenstein

Betriebszeiten: 9.00–16.15 Uhr

#### Luftseilbahn Stoos–Fronalpstock

Kein Winterbetrieb.
NOTES