Abstracts of ESR & ER speeches

3rd Meeting of RTN 'Hydrogen' Warsaw 22–25.10.2009

22.10.09 THU

Solar Driven Water Splitting: Principle and An Example with Hematite

Florian Le Formal

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Dihydrogen is often seen as a very promising energy vector for the future in a carbon-neutral market. An efficient and sustainable way to produce this fuel would be to use our most abundant renewable source, the Sun, to provide the energy required to split water molecules into dioxygen and dihydrogen.

Among all semiconductors that fulfill the solar water splitting criteria, hematite (a-Fe_2O_3 or rust) is an interesting candidate because of its chemical stability in aqueous environments, its matchless abundance and its favorable band gap (2.0 - 2.2 eV). Additional energy is nevertheless needed to account for the too low conduction band edge compare to the water reduction potential; this additional bias can be brought by another solar cell for example.

Other important limitations for the use of iron oxide in solar water splitting system are the fall off in the absorption at the long wavelengths (close to the band gap) and rapid electron-hole recombination due to the short diffusion length of charge carriers. To minimize these limitations, very thin layers of iron oxide can be used in order to decrease the distance between where the light is absorbed (= where the charge carriers are activated) and the interface with the electrolyte (=where the charge carriers are reacting). To keep high light harvesting, this thin film can be deposited on a mesoporous and conductive material in a host-guest configuration.

The presentation at the Warsaw RTN meeting 2009 will focus on the efforts to achieve iron oxide thin films photoactive and efficient in solar water splitting. A new pretreatment of the substrate with TEOS (Tetraethyl orthosilicate) spray has shown a drastic effect on the iron oxide thin film photoactivity and will also be discussed.

Innovative nanostructured photoanodes for solar energy conversion

Jeremie Brillet

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Direct splitting of water by a photoelectrochemical (PEC) tandem cell provides a means to convert energy from our most abundant renewable source, the Sun, into dihydrogen, which could then be employed as an energy vector in a carbon-neutral market [1]. The first demonstration of water splitting was made with a semiconductor-liquid junction (SCLJ) using TiO_2 as a photoanode by Fujishima in 1972 [2]. Hematite (α-Fe_2O_3) has a well-suited band gap of 2.1 eV, is largely available and is stable in aqueous environment making it a good candidate as a photoanode material. As a drawback, hematite has a very short hole diffusion length (2 – 4 nm) [3] as compared to the light penetration depth (α^{-1} = 118 nm at λ = 550 nm) [4]. This causes most photons to be absorbed in the bulk far from the SCLJ, creating photogenerated holes with low probability of participating in water oxidation. To answer this problem, we present here an innovative strategy that simultaneously amplifies the harvesting of photons and improves charge collection in a new kind of nanostructured composite electrode, where a thin film of Fe_2O_3 is conformaly coated on a three-dimensional transparent conductive backbone.

[1] Turner, J. A. *Science* **2004**, *305*, 972.

[2] Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.

[3] Kennedy, J. H.; Frese, K. W. *J. Electrochem. Soc.* **1978**, *125*, 709.

[4] Balberg, I.; Pinch, H. L. *J of Magn. Mater.* **1978**, *7*, 12.

Exploration of a new class of p-type oxides for hydrogen evolution in photoelectrochemical water splitting

Adriana Paracchino

Ecole Polytechnique Federale de Lausanne

Solar hydrogen production using semiconductors materials interfaced to an aqueous electrolyte is attracting much attention since the first report on this phenomenon in the early 70s[1]. The key of the process lies in the semiconductor/electrolyte interface.

Photocatalytic or photoelectrochemical hydrogen evolution using visible light can be observed only if the semiconductor meets certain requirements as to band gap value and band edges position. It is often the case that one material matches either the water-to-hydrogen reduction potential or the water-to-oxygen oxidation potential, so that it can drive half of the water splitting reaction if suitably biased in a photoelectrochemical cell (PEC). Oxides are usually good candidates because of their stability in water and n-type oxides have been widely explored for water oxidation. Conversely, there are few examples in the literature of stable p-type materials as photocathodes.

In this study we focus on delafossite-structure oxides $CuBO_2$, where B is a trivalent cation such as Al^{3+} or Cr^{3+}, which seem promising as to the above-mentioned requirements. These materials have been explored in the last decade as p-type conductors but there isn’t any reference in the literature about their use as photocathodes. The synthesis and the photoelectrochemical characterization of $CuAlO_2$ and $CuCrO_2$ are presented and discussed. PEC activity is proved and measured by photocurrent transients under chopped visible light at fixed potentials, in a three-electrode cell. As expected, the synthesis route plays an important role on the photoactivity, probably fixing the holes content of the material and then its conductivity. These intrinsic holes have been identified as ionized copper vacancies [2]. The photocurrent doubles when the material is irradiated with UV light, as a consequence of a direct band gap absorption at around 3.5 eV. The photocurrents are of the order of 100uA/cm^2 for both $CuAlO_2$ (Fig.1) and Ca-doped $CuCrO_2$ but smaller for undoped $CuCrO_2$

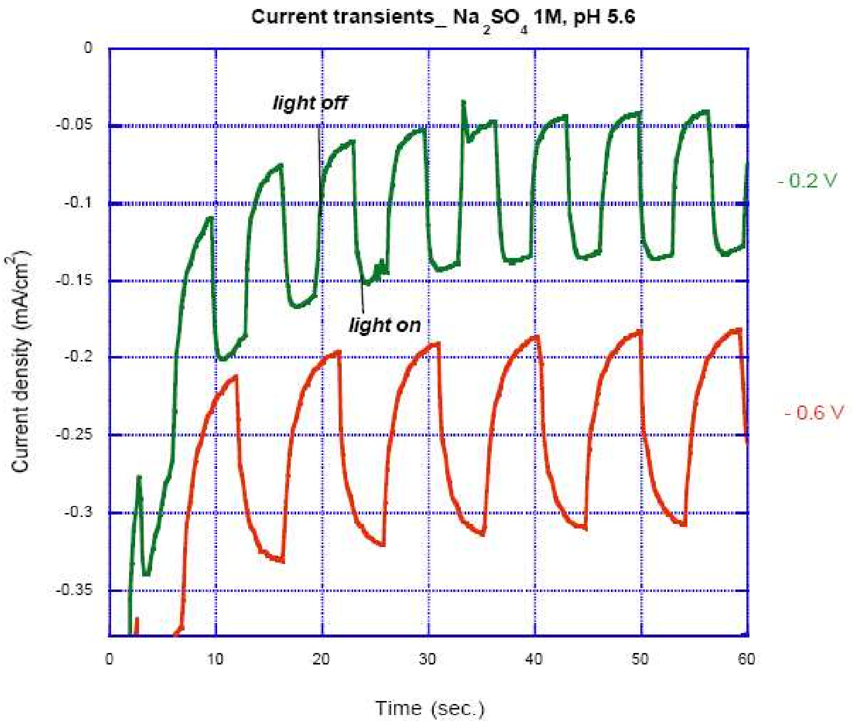


Fig.1: Time-dependant photoelectrochemical response under light on/of illumination at a constant applied potential for CuAlO$_2$ photocathode.

A major problem is the big dark current of the photocathodes, whose cause is still unclear.

References

1- Fujishima A, Honda K Nature 1972, 238, 72

2- Ueda K, Hase T, Yanagi H, Kawazoe H, Hosono H J.Appl.Phys. 2001, 89, 70

Nanostructuring Photoanodes for Hydrogen Production via Water Splitting

Rafael Martins

Chalmers University of Technology

Self-interaction Corrected Energy Functionals --An interpolating between two regimes of electronic structure.

Peter Kluepfel

University of Iceland

Density Functional Theory (DFT) within the Kohn-Sham (KS) scheme and based on the local density approximation or generalized gradient approximations is the most widely used electronic structure theory for the calculation of total energies and geometries. Since years it has been successfully applied both, to solid-state systems and isolated atoms.

However, the reliability of KS-DFT is hampered whenever the electronic structure can not be assumed to be build up from fully delocalized (metallic) electrons or fully localized (atomic) electrons. Worst case scenarios are periodic systems with defects. But even surfaces or the very simple case of anatomic bond already unfold the intrinsic problems of KS-DFT.

Self-interaction corrected energy functionals (SIC-DFT) are a promising approach to build a formal link between both system classes by providing a self-consistent interpolation.

Examples ranging from diatomic molecules to small clusters will be given, illustrating why and when KS-DFT works or fails and how the deficiencies can be overcome by self-interaction correction.

Cluster study of the photooxidation of water on rutile titanium dioxide (TiO_2).

Álvaro Valdés

Universiteit Leiden

The photooxidation of water on the rutile TiO_2 (110) surface is investigated using density functional theory (DFT) calculations. A stable $(TiO_2)_{26}$ cluster (see Fig. 1) is used to model the rutile bulk and (110) surface. A model in which every reactant state contains a photoinduced positively charged cluster and every product state contains a neutral cluster plus a proton is used to study the photooxidation of water. In each reaction step, a photoinduced hole localized in the surface reacts with an adsorbed atom or molecule surrounded by water leading to a neutral cluster, a proton surrounded by water, and a product vacancy, adsorbed atom or molecule. According to this model the illumination of the TiO_2(110) surface with light provides enough overpotential for the photooxidation to proceed spontaneously.

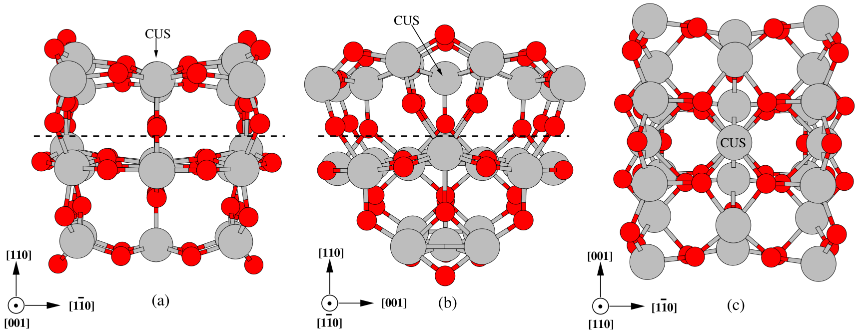


Figure 1: Two side (a, b) views and the top (c) view of the $(TiO_2)_{26}$ cluster. Atoms below the dashed line in the side views are kept frozen in the surface relaxations. Light grey spheres represent metal ions and red spheres represent oxygen atoms.

Competitive Chlorine and oxygen evolution at rutile(110) surfaces (DFT)

Isabela Man

Technical University of Denmark

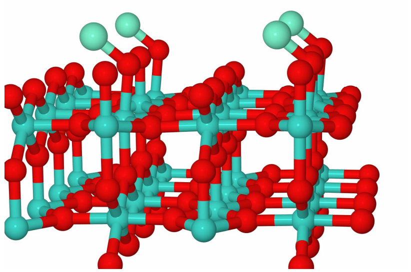
As a starting point I will make an introduction to few notions that lead these calculations. First “mechanics” as used in physics is traditionally the study of the behavior of bodies under the force like: gravity. Molecules are made of nuclei and electrons, and quantum mechanics deals, **fundamentally** with the motion of electrons under the influence of electromagnetic forces exerted by nuclear charges. An understanding of behavior of electrons in molecules and thus the structures and reactions of molecules rests on quantum mechanics. There are a number of methods that try to calculate the geometry and energies of molecules. **Density Functional Theory (DFT)**, it is a method that address this problem, by considering the so called the electron probability density (the probability of finding an electron in a volume element).

Chlorine–alkali industry is one of the major industrial electrochemical technologies, which consume a significant fraction of electrical energy. The reversible potential for Cl_2 evolution is higher than for O_2 evolution; consequently O_2 evolution should be preferred in brine solutions:

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e \qquad E^0 = -1.36$ V

$6H2O(l) \rightarrow O_2(g) + 4H_3O^+(aq)+4e \qquad E^0 = -1.23$ V

Judging by the values of E^0, water should be slightly more readily oxidized than chloride. However in practice Cl_2 is actually produced in preference to O_2. In industry the best used electro catalyst it is Dimensional Stable Anode (DSA) which is a mixture of rutile oxides: TiO_2, RuO_2, IrO_2. The idea of this work it is, to start from the electronic energies given by DFT calculations of different species that could form as intermediates during chlorine evolution (on the most stable surface(110) of these oxides). We applied different corrections in order to find the free energy of these reactions. We will construct stability diagrams(across the pH and oxygen binding energies) of these surfaces and volcano plots for different proposed mechanisms in order to make predictions for catalyst activity. All these analysis will allow us for example to predict zones that will allow only oxygen evolution, for example if one want to produce oxygen from sea water.

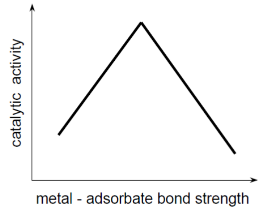


The structure of the rutile (110) surface, that is active for oxygen and chlorine evolution

Other key words:

Catalyst – breaks and lets other bonds form easier.

Volcano plots: -predict activity of a catalyst function of catalyst adsorbate interaction (not too strong, not too weak)



Towards Understanding Mechanism of Reversible Hydrogen Storage in Transition Metal Doped Sodium Alanate

Ivan Ljubic

Oxford University

On the basis of density functional theory and coupled-cluster CCSD(T) calculations we propose a mechanism of the dehydrogenation of transition metal doped sodium alanate. Insertion of two early 3d-transition metals, scandium and titanium, is compared, both of which are promising catalysts for reversible hydrogen storage in light metal hydrides. The mechanism is deduced from studies on decomposition of a simple model system consisting of one transition metal atom and two $NaAlH_4$ units. Subsequently, the significance of such minimal cluster model systems to the real materials is tested by embedding the model systems into the surface of the $NaAlH_4$ crystal. It was found that the dehydrogenation proceeds via breaking of the bridge H-Al bond and consequent formation of intermediate coordination compounds in which the H_2 molecule is side-on (η^2-) bonded to the transition metal centre. The overall barrier to the H_2 release is thus dependent upon both, the strength of the Al-H bond to be broken, and the depth of the coordinative potential. The analogous mechanism applies for the recognized three successive dehydrogenation steps. The gas-phase model structures embedded into the surface of the $NaAlH_4$ crystal exhibit an unambiguous kinetic stability and their general geometric features remain largely unchanged.

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23.10.09 FRI

The “Boron effect” in the decomposition of light metal borohydride

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EMPA

The purpose of this work is an investigation of the “boron effect” on the kinetics of dehydrogenation for alkali and earth alkali borohydrides (MBH_4) under hydrogen pressure at non-isothermal condition (non-equilibrium). As reported in our previous study [1], the addition of boron to the $LiBH_4$ decreases the dehydrogenation temperature by 150 °C (Fig. 1). This effect is due to the formation of new intermediates. Experiments are carried out using a magnetic suspension balance [2], differential scanning calorimetry (DSC) [3] and mass spectroscopy [4].

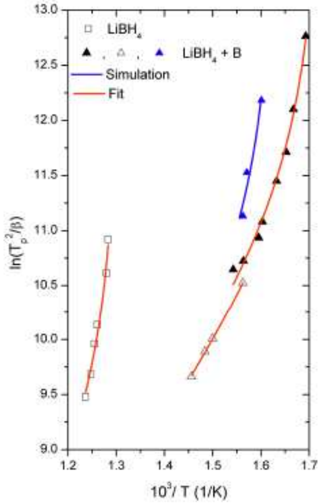

Fig. 2: $\ln(T^2/\beta)$ vs 1/T for the decomposition of $LiBH_4$ and $LiBH_4$+B under 1 bar H_2 at various heating rates.

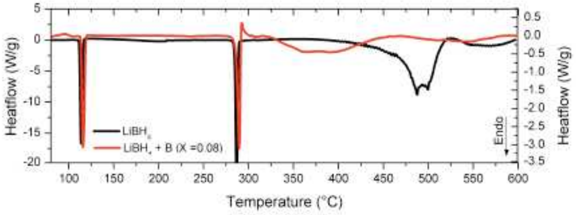

Fig. 1: DSC traces for $LiBH_4$ (black line) and $LiBH_4$+B (red line) under 1bar H_2 at 11 °C/min.

Additionally, the kinetic parameter of activation energy is usually evaluated by plotting the rate maxima measured in a so-called Kissinger plot [5]. However, this procedure fails, when finite pressures are applied. We propose a model (below) to calculate the "true" activation energy and taking into account the effect of hydrogen pressure [3] (Fig. 2).

$$\ln\left(\frac{T_p^2}{\beta}\right) = \frac{E_a^*}{RT_p} - \ln\left[1 - \frac{p}{\exp(-\frac{\Delta H_r}{RT_p} + \frac{\Delta S_r}{R})}\right]$$

[1] F. Pendolino et al. Phys. Chem. C, p 17231, v. 113 (2009)

[2] http://www.ruhr-uni-bochum.de/thermo/Forschung/Seiten/magnetschwebewaagen-eng.htm

[3] http://en.wikipedia.org/wiki/Differential_scanning_calorimetry

[4] http://www.chem.arizona.edu/massspec/

[5] H. E. Kissinger. Anal. Chem. p. 1702, v. 29 (1957)

[6] Laidler , Chemical Kinetics Edition 3

Storage of hydrogen in lightweight $Y(BH_4)_3$.

Tomasz Jaroń

The University of Warsaw

Fourteen different synthetic approaches towards pure solvent-free $Y(BH_4)_3$ have been tested, thirteen of which have failed. Attempted reactions of YCl_3 or $Y(OC_4H_9)_3$ with $LiBH_4$ in THF, those of YCl_3 with $(C_4H_9)_4N^+ BH_4^-$, as well as between $YH_{x\sim3}$ and R_4NBH_3 (R = CH_3, C_2H_5) in the presence or absence of a solvent (n–hexane or CH_2Cl_2) did not lead to the expected product. The mechanochemical solid/solid reactions ($MBH_4 + 3\ YX_3 \rightarrow Y(BH_4)_3 + 3\ LiCl$, where M = Li, Na; X = F, Cl) have succeeded only for the $LiBH_4$ and YCl_3 reagents, but the separation of the crystalline reaction products ($Y(BH_4)_3$ in its P–3a phase and LiCl) by dissolution or floatation in various solvents has not been successful.

The thermal decomposition process of $Y(BH_4)_3$ in mixture with LiCl has been investigated with thermogravimetric (TGA) and calorimetric analysis (DSC) combined with the spectroscopic evolved gas analysis (EGA). Three endothermic steps could be distinguished in the DSC profile (up to 500 °C) at *ca.* 232, 282, 475 °C (at a heating rate 10 K/min) corresponding to the three steps of thermal decomposition. The first thermal decomposition step is partly overlapped with a phase transition. Solid decomposition products are amorphous except for the new cubic β polymorph of $Y(BH_4)_3$ (F-43c) overlooked in the previous work. The high–temperature β phase forms at the onset of thermal decomposition of the low-temperature P–3a α form and it may be prepared by heating of the low–temperature phase up to a quite narrow temperature range (194–216 ºC) followed by rapid quenching to room temperature. Assignment of the F-43c unit cell to the HT-$Y(BH_4)_3$ polymorph was supported by the DFT calculations. According to calculations of the phonon dispersion, the F-43c structure is kinetically stable (a metastable phase) at low temperatures.

The thermal decomposition of the HT-$Y(BH_4)_3$ phase differs from that of LT-$Y(BH_4)_3$ only as far as the first step of decomposition is considered. The shoulder of the first DSC peak (at *ca.* 195 °C, corresponding to the α→β transition) is obviously absent, and the peak corresponding to thermal decomposition is shifted to lower temperatures (by *ca.* 10 °C), as expected for a less-thermodynamically-stable phase.

$Y(BH_4)_3$ constitutes a novel highly efficient hydrogen storage material (theor. 9.1 wt % H). Since evolved H_2 is slightly contaminated by toxic boron hydrides and products of their pyrolysis, purification of H_2 gas is needed for any applications.

Probing hydrogen storage properties of materials based on yttrium and ytterbium.

Radostina Genova

The University of Warsaw

Yttrium compounds

Ammonia borane (AB, NH_3BH_3) contains ~19.6 wt.% of hydrogen and has been considered as an important hydrogen storage material[i]. The molecule of AB consists of hydridic B–H and protic N–H parts and a strong B–N bond that makes hydrogen evolution from solid more favorable than Brønsted dissociation to ammonia (Lewis base) and diborane (Lewis acid). Interestingly, AB may serve itself as an acid in its reactions with strong ionic Lewis bases (such as LiH, NaH, CaH_2 and possibly also MgH_2) while forming metal amidoboranes. Our initial research was triggered by the opportunity to affect the temperature of decomposition of the light weight hydrogen storage material NH_3BH_3, by doping it with YH_3 using disk–milling.

YH_3 was synthesized from metallic yttrium and H_2 in PCT Pro-2000 equipment (20bar, 300ºC, 162hrs). We investigated the thermal decomposition of YH_3-doped NH_3BH_3 using simultaneous thermogravimetry (TGA) and differential scanning calorimetry (DSC), mass spectroscopy, FTIR, and elemental (combustion) analysis. Due to lack of catalytic effect on the thermal decomposition of ammonia-borane we have targeted synthesis and tested the hydrogen storage properties of related yttrium amidoborane $Y(NH_2BH_3)_3$.

Up to now the amidoboranes of trivalent elements have not been reported in the literature. In the present work we focused on synthesis and characterization of Y derivative. We are interested whether this compound could exhibit H_2 storage properties superior to known amidoboranes of mono– and divalent cations. Expected hydrogen content of $Y(NH_2BH_3)_3$ is as large as 8.4 wt.%. Of course, one might think of scandium amidoborane, $Sc(NH_2BH_3)_3$ with theoretical hydrogen content of 11.1 wt.%, but scandium is rare and prohibitedly expensive.

We have attempted synthesis of $Y(NH_2BH_3)_3$ via five different 'dry' pathways:

$$YH_3 + 3NH_3BH_3 \rightarrow Y(NH_2BH_3)_3 + 3H_2\uparrow \qquad (1)$$

$$YCl_3 + 3LiNH_2BH_3 \rightarrow 3LiCl + Y(NH_2BH_3)_3 \qquad (2)$$

$$YCl_3 + 3NaNH_2BH_3 \rightarrow 3NaCl + Y(NH_2BH_3)_3 \qquad (3)$$

$$YF_3 + 3NaNH_2BH_3 \rightarrow 3NaF + Y(NH_2BH_3)_3 \qquad (4)$$

$$YF_3 + 3LiNH_2BH_3 \rightarrow 3LiF + Y(NH_2BH_3)_3 \qquad (5)$$

We tried to reach $Y(NH_2BH_3)_3$ via methathetic reactions (eq. 2–5) from different mixtures of yttrium halide and alkali metal amidoborane in a molar ratio 1:3 milled for 9 min (3 times 3 min with 5 min breaks) in the WC disc mill. Obtained composites were subject of thermal analysis, X-ray diffraction(XRD) and Infra Red spectroscopy(IR) analyses.

Crystalline $Y(NH_2BH_3)_3$ was successfully obtained as a product of the reaction (2). Reflections of a new phase in the XRD appeared together with the peaks of LiCl. After indexing the new peaks as a possible solution has been found C-centered monoclinic crystal unit cell C2/c with volume 1533.25(17) A^3 which yields the volume per formula unit of $Y(NH_2BH_3)_3$ of 191.7 A^3 (Z=8). Amorphous form of $Y(NH_2BH_3)_3$ was synthesized in a similar reaction utilizing $NaNH_2BH_3$ and YCl_3.

Thermal decomposition of the title compound takes place in the range of 80–300ºC. Several small exothermic signals are present in the DCS profile. Thermal decomposition of the sample seems to be very complex. Total mass loss is 5.5% and it is slightly larger than the theoretical hydrogen content of the composite (4.9%). Qualitative analysis of the gases evolved show that hydrogen is contaminated with significant amount of ammonia.

Reactions (1), (3), (4) and (5) did not lead to any new crystalline phase in the XRD spectra. Products of these reactions are very different from one another so is their thermal decomposition. However, in all cases the evolved hydrogen is polluted with ammonia and the thermal decomposition is exothermic (and thus irreversible). Presence of NH_3 in H_2 gas is undesirable for on–board hydrogen storage in a tandem with low-temperature fuel cell (FC) applications.

Ytterbium compounds:

Ytterbium thin films has been investigated as a potential catalyst for hydrogen storage using QCM-equipment (Quartz Crystal Microbalance) (please *cf.* Nicola's talk for more details). In order to prevent the oxidation of Yb from the atmospheric oxygen we covered it with 10nm of Pd and to prevent alloying between Yb and Pd and Yb and the gold electrodes of the QCM crystal we sandwiched the Yb layer between two Ti layers with thickness of 10nm each.

Samples have been analyzed by XPS (X-ray Photoelectron Spectroscopy), AFM. XPS have been used to detect the amount of oxygen in the Yb layer and to detect expected differences in the Yb peaks due to its hydrogenation.

Abbreviations of the techniques used:

TGA – thermogravimetric analysis

DSC – differential scanning calorimetry

IR – infra-red spectroscopy

XRD – X-ray powder diffraction

QCM – quartz crystal microbalance

XPS – X-ray photoelectron spectroscopy

AFM – atomic force microscopy

Synthesis and characterization of Al/ZIF-8 composites using Quartz Crystal Microbalance (QCM).

Ewa Banach

Shell

H_2 dissociation and formation of AlH_3 on *c(2×2)*-Ti/Al(100) surfaces

Jian-Cheng Chen

Leiden University

One of the open question remains in hydrogen storage is how catalysts like Ti improve the kinetics and reversibility of hydrogen absorption in and release from the complex metal hydride sodium alanate ($NaAlH_4$).

Recent paper by us [Chen, *et.al*.**,** *JPCC* 113*(***2009)**11027] has showed that the most energetic favorable model for H_2 dissociation is on a 1 ML Ti covered *c(2×2)*-Ti/Al(100) surface with Ti in the first and third layers. A six-dimensional potential energy surface (PES) has been built on the slab model by GROW method [Collins, *Theor. Chem. Acc.*, 108(**2002**)313] and therefore the H_2 dissociation rates has been calculated by both quasi-classical trajectories and time-dependent wave-packet (TDWP) method. The basic idea of the GROW method is to use a statistic tool called Bayesian analysis to define a confidence radius and to interpolate the potential value. In the quantum TDWP method, one of the key points is to solve the time-dependent Schrödinger equation by split the six dimensional Hamiltonian to get small errors $O(\Delta t^3)$, which is call split operator (SPO).

Meanwhile, the wave function is expanded by orthogonal basis sets for X, Y, Z, r, θ and φ, in which, the degrees of freedom in X, Y, Z, r use plane-wave basis sets (Fourier representations) and the degrees of freedom in θ, φ use spherical harmonics of the Legendre polynomials (Gauss-Legendre representations).

After H_2 dissociation on the Ti/Al(100) surface, one possibility is to form AlH_3 or other complex like Al_2H_6. A paper by Gunaydin *et.al*. [*PNAS*, 105(**2008**)3673] suggests that the diffusion of AlH_3 could be the rate limited step in the dehydrogenation of $NaAlH_4$. Thus, we are focusing on the formation of AlH_3 from the H-covered Ti/Al(100) surfaces at this moment.

Molecular Catalysts for Thermal Decomposition of Complex Hydrides

Andrew Churchard

The University of Warsaw

A large variety of bulk transition metal catalysts (for example TiO_2, Fe_2O_3, or $TiCl_3$) have been used in the past to enhance hydrogen uptake and evolution from efficient hydrogen storage materials. Here we investigate novel candidates for molecular catalysts, with the aim of capitalizing on their potential advantages over bulk catalysts in respect of a greater availability of active sites, more efficient dispersal in the storage material and reduction in milling time needed for mechanochemical doping.

The methodology focuses on first synthesizing and characterizing the novel compound followed by investigation of its catalytic properties. Characterisation consists of x-ray diffraction, IR spectroscopy and simultaneous thermal TGA/DSC analysis with concomitant FT-IR and mass spectrometry of evolved gas for deuterated and non–deuterated systems. Catalytic properties are investigated by introducing the catalyst to the hydrogen storage material through disc milling or wet chemistry methods and subsequent examination of the products.

Our attention has focused on 1,4,8,11-tetraaza-cyclotetradecane (cyclam) chelate complexes of Ni(II) as their reduced form, containing Ni(I), is capable of the formidable task of CO2 activation, as shown by Sauvage et al [1]. CO_2 and H_2 are notably similar in some important physical characteristics [2].

Thermal stability and properties of both cis- and trans-Ni(cyclam)$(BH_4)_2$ as well as the outcome of reactions between Ni(cyclam)(SO_4) or Ni(cyclam)$(ClO_4)_2$ and MAlH4 (M = Li, Na) will be discussed in the present contribution.

The following Wikipedia pages all provide a useful introduction the relevant techniques included in this talk:

X-ray diffraction: http://en.wikipedia.org/wiki/X-ray_crystallography

IR spectroscopy: http://en.wikipedia.org/wiki/IR_spectroscopy

TGA: http://en.wikipedia.org/wiki/Thermogravimetric_analysis

DSC: http://en.wikipedia.org/wiki/Differential_scanning_calorimetry

Mass spectrometry: http://en.wikipedia.org/wiki/Mass_spectrometry

References

[1] M. Beley, J.-P. Collin, R. Ruppert, J.-P. Sauvage, *Chem. Commun.* 104, 1984, 1283.

[2] W. Grochala, *Phys. Chem. Chem. Phys.* 8, 2006**,** 1340.

Investigating hydrogen storage in thin films and nanoparticles using Quartz Crystal Microbalance (QCM)

Nicola Naujoks

Chalmers University of Technology

Reducing the geometrical dimensions of hydrogen storing materials to the nanoscale is expected (and shown) to result in advantageous thermodynamic and kinetic properties. Studying this effect, however, demands highly sensitive measurement techniques. One approach to investigate the hydrogenation properties of thin metal films and nanostructured metal particles is the use of a Quartz Crystal Microbalance (QCM). By detecting shifts in resonance frequency the QCM enables the measurement of minute mass changes occurring during hydride formation, corresponding to a fraction of monolayer of hydrogen atoms. A good reference for understanding the basic principle of QCM can even be found on Wikipedia: http://en.wikipedia.org/wiki/QCM.

To be studied in a QCM setup, the sample structures have to be fabricated onto the surface of quartz sensor, see figure 1. The feasibility of the QCM technique to investigate hydrogenation of thin metal films is demonstrated at the example of a Pd covered 100nm thick Mg film, where we obtained thermodynamic data in term of pressure-composition-isotherms.

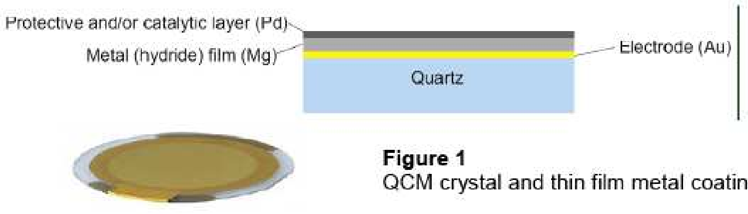

Figure 1
QCM crystal and thin film metal coating

Based on studies performed regarding the hydrogenation of Ytterbium (Yb) (see figure 2), I will demonstrate how QCM investigations can help to obtain thermodynamic (and to a certain extent even kinetic) data of thin film metal hydrides. I will furthermore show up some (current) limitations of this method, as well as ways to solve them.

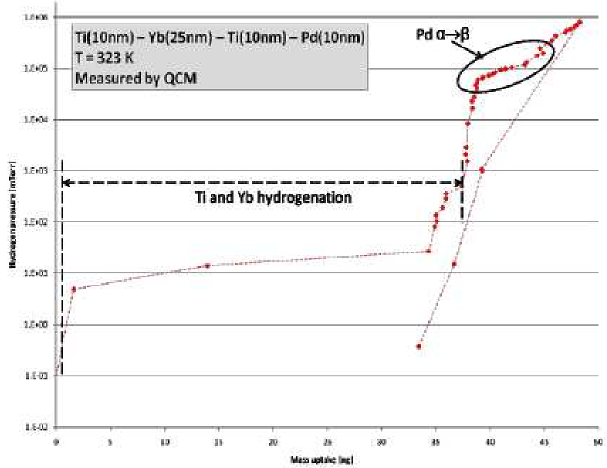

Figure 2

PCI diagram obtained on 25nm Yb film (capped with Ti and Pd) @ 50 C. QCM sensor: 10 MHz fundamental frequency, 3rd overtone.

Recommended literature

Hydrogen storage in nanoparticles: Berube V, Radtke G, Dresselhaus M and Chen G 2007 Int. J. Energy Res. 31 637–63. And presentation by Igor Zoric in Warsaw! Hydrogen storage in thin metal films: A. Remhof, A. Borgschulte, *Thin-Film Metal Hydrides*, ChemPhysChem 2008 (9) 2440.

QCM and hydrogen storage: I. Kulchytskyy et al, *Direct mass determination of hydrogen uptake using a quartz crystal microbalance,* Appl. Phys. Lett. 91, 113507 (2007).

3-D Porous Templates to Study Hydrogen Storage in Nanoparticles by QCM

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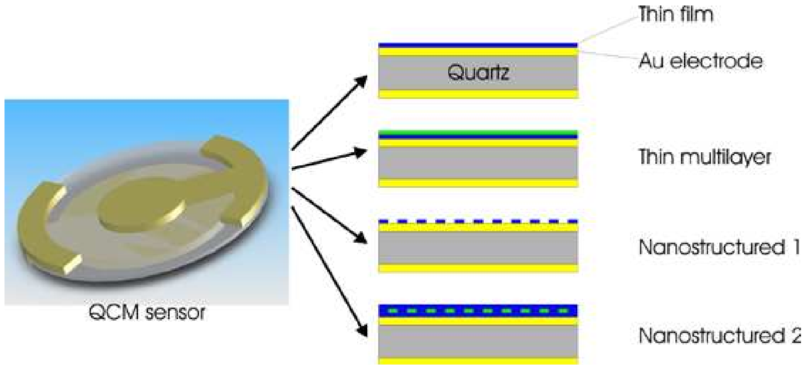
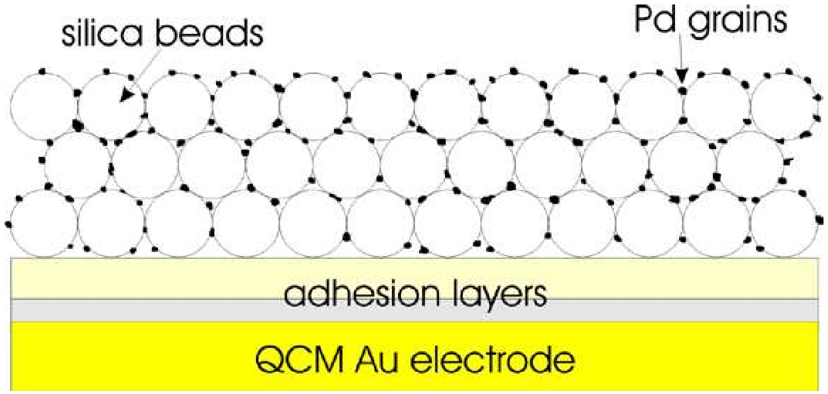
The quartz crystal microbalance (QCM) is a sensitive tool to measure small mass changes. In our group at Chalmers we are using it to study hydrogen adsorption in materials. As we decrease the grain size of the hydrogen storing material, the surface/volume ratio increases very much, thus we expect better kinetics (i.e. faster absorption/desorption). Meanwhile, below a certain threshold, even the thermodynamics of the process can change. Therefore it is interesting to study hydrogen absorption-desorption in nanostructured storage materials. Nanostructuring can be done in 1, 2, or all the 3 dimensions.



A one dimensional nanostructuring way is to decrease the deposited film thickness. This thin film then can be shaped further in the remaining other two dimensions. When fabricating 3-D nanostructures on a QCM crystal surface, the area of the crystal's surface is limiting the total mass of the deposited material, hence, the total mass of the absorbed hydrogen, and thus, the final signal strength. In order to increase the detected signal, we need to find a way to deposit more individual nanoparticles than the surface area would allow. One way of doing this is to use a porous template material. We chose 20 nm silica beads for this. They can be deposited in several layers, in a reproducible thickness. The surface and the voids between the silica spheres can accommodate the active material. First we tried this with palladium, deposited from a Pd(II) complex solution followed by reduction in hydrogen atmosphere. A big advantage of this porous template concept is that hydrogen storage materials can be easily deposited from solutions, there is no need for expensive equipments or experimental conditions very far from ambient temperature and pressure.



Recommended reading: the article 'QCM' on Wikipedia.