



# HYDROGEN STORAGE IN NEW COMPLEX HYDRIDES (COMPHY)

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Autor und Koautoren	Andreas Züttel, Pascal Martelli
beauftragte Institution	EMPA Dübendorf, Abt. 138 Hydrogen & Energy
Adresse	Überlandstrasse 129, CH-8600 Dübendorf
Telefon, E-mail, Internetadresse	+41 44 823 4038, andreas.zuettel@empa.ch, <a href="http://www.empa.ch/h2e">www.empa.ch/h2e</a>
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### ABSTRACT

Complex hydrides i.e. alanates (e.g.  $\text{Na}[\text{AlH}_4]$ ) as reversible hydrogen storage materials were first described by Boris Bogdanovic in 1996 at the MH96 conference in Les Diablerets, Switzerland. In 2001 Züttel and coworkers have started to investigate related complexes the boranates (e.g.  $\text{Li}[\text{BH}_4]$ ) as hydrogen storage materials. The boranates offer a much greater gravimetric hydrogen density as compared to the alanates. The hydrogen absorption and desorption mechanism as well as the role of the catalyst are still not known. Therefore, the local environment of the catalyst e.g. Ti-atom is investigated by means of EXAFS (extended x-ray absorption fine structure) and Raman spectroscopy. Furthermore, the structure of the complex ion e.g.  $[\text{BH}_4]$  during the hydrogen desorption is investigated and the hydrogen dynamics in the lattice is modelled. These measurements are supplemented by UV-vis spectroscopy and isotope exchange experiments (hydrogen-deuterium). The final goal of the project is to describe the mechanism of the hydrogen sorption reaction in great detail together with the physical properties of the compounds as a function of the hydrogen concentration. This work represents also the contribution to the IEA Task 22.

## Projektziele

### Workpackage 1: Local environment of the catalyst

Titanium is used in  $\text{Na}[\text{AlH}_4]$  as a catalytic active additive for the thermal desorption of hydrogen at temperatures far below the melting temperature. However, since the discovery of the catalyst in 1996 and despite an extensive research activity the role of the catalyst is still not known. It is not even known in what chemical state the catalyst acts. Therefore, a local probe like EXAFS allows to investigate the chemical state and the local environment of the catalyst in-situ and the results lead to a better understanding of the mechanism. EXAF experiments at the synchrotron (SLS, PSI) on model complexes like  $\text{Na}[\text{AlH}_4]$  during the hydrogen desorption will be carried out and the chemical state as well as the local environment will be described during the hydrogen desorption reaction.

### Workpackage 2: Local structure of $[\text{BH}_4]^-$

The stability of the  $[\text{BH}_4]^-$  strongly depends on the localisation of the electron on the boron atom. Therefore, the structure of the  $[\text{BH}_4]^-$  is crucial for the desorption mechanism. Raman spectroscopy allows to investigate the relevant vibrational modes of hydrogen and deuterium. These vibrational modes are analyzed and semi-empirical models are developed for the stability of the complex hydrides.

### Workpackage 3: Hydrogen diffusion

Hydrogen in the solid appears always in atomic form. However, during the desorption a hydrogen molecule is formed. For metallic hydrides with a well defined lattice and surface the hydrogen diffuses through the lattice of the host metal to the surface and recombines at the surface to form a molecule. However, in a complex hydride the hydrogen diffusion is not understood nor is the surface in the multiphase system upon desorption defined. Therefore, the hydrogen diffusion is investigated by quasielastic neutron scattering and the diffusion sites as well as the hoping frequency are measured and related to the activation energy.

### Workpackage 4: Vibrations and excitations

The distribution of the electrons between the constant atoms in the complex hydrides is defining the physical properties of the materials. By means of in-situ UV-vis-IR spectroscopy the electronic properties of the complexes is probed as well as the vibrational excitations. Therefore, its possible to investigate the materials during the desorption process independent of the crystal structure, i.e. also in the molten state. This leads to a completely new understanding of the relevant processes during hydrogen desorption.

### Workpackage 5: Mobility of the hydrogen in the lattice

The local hydrogen mobility does not necessarily allow a transport of the hydrogen atoms through the lattice. Only the isotope exchange experiments where the hydrogen is replaced by deuterium is a true measure of the mobility of hydrogen in the host lattice. The exchange of deuterium with hydrogen and vice versa allows the investigation of the global mobility of hydrogen and a empirical description of the diffusion process.

## Durchgeführte Arbeiten und erreichte Ergebnisse

We report first principles studies of the role of titanium in the bulk and surface of sodium alanate.

Our studies confirm that neutral titanium atoms are energetically unstable when incorporated into the bulk  $\text{NaAlH}_4$  but neutral  $\text{Ti}^{4+}$  cations are the most stable on the surface. On the contrary  $\text{Ti}^{1+}$  cations are energetically favorable in the bulk, under certain conditions. The most stable configuration is for the interstitial  $\text{Ti}^{4+}$ . Neutral sodium and

hydrogen vacancies are not stable neither in the bulk nor on the surface. Our studies explain that high oxidation states of Ti are crucial for its catalytic activity.

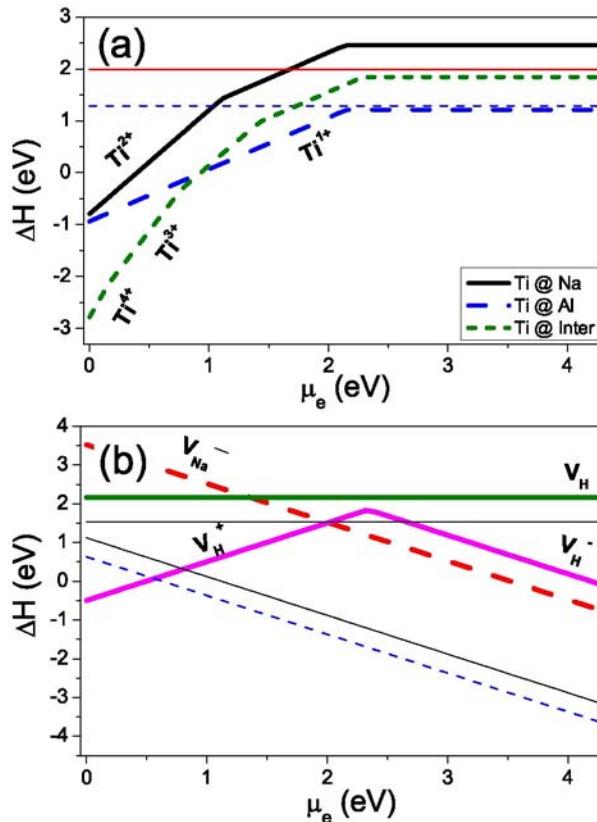


FIG. 1: Formation enthalpy of Ti incorporated in  $\text{NaAlH}_4$  (a). Na and H vacancies  $\text{NaAlH}_4$  (b). Thick lines refer to the bulk, thin lines are for the (001) surface. Plots are shown for H-rich ( $\mu(H) = 0$ ).

#### Paper:

[1] Zbigniew Lodzianna, Andreas Züttel, „Ti cations in sodium alanate”, J. Alloy Comp. accepted

#### Präsentationen:

#### Nationale Zusammenarbeit

- Prof. Bruce Patterson (SLS &ETHZ) for synchrotron diffraction measurements
- Prof. R. Nesper (ETHZ) for the synthesis of specific materials

#### Internationale Zusammenarbeit

- Prof. Shin-Ichi Orimo, Tohoku University in Sendai, Japan.

#### Bewertung 2007 und Ausblick 2008

Project has just started 2 months ago. Pascal Martelli our new PhD student will work the first 6 months on the project and subsequently Dr. Robin Gremaud will continue as a Post. Doc.

#### Referenzen

- [1]