BOR4STORE – Fast, reliable and cost effective boron hydride based high capacity solid state hydrogen storage materials

K. Taube[1], G. Capurso[1], J. M. Bellosta v. Colbe[1], C. Pistidda[1], M. Dornheim[1], T. Guerrero Cervera[2], D. Márquez Gómez[2], I. Castellano Moreno[2], H. Zoz[3], D. Yigit[3], R. Keder[4], M. Krovacek[4], T. Jensen[5], B. Richter[5], B. Hansen[5], B. Hauback[6], S. Deledda[6], O. Zavorotynska[6], M. Baricco[7], J. Vitillo[7], E. Pinatel[7], A. Züttel[8], A. Borgschulte[8], N. Stadie[8], A. Stubos[9], G. Charalambopoulou[9], T. Steriotis[9], A. Yiotis[9]

1. Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research 2. ABENGOA HIDROGENO 3. Zoz Group 4. 5. AARHUS UNIVERSITY 6. IFE 7. NIS 8. EMPA 9.

General

Funded by the European "Fuel Cells and Hydrogen Joint Undertaking"

- Total Budget 4.07 Mio.€, total funding 2.3 Mio. €.
- runtime April 2012 to September 2015

Scientific understanding of boron based hydrogen storage materials (>8wt.%)

- Reaction mechanisms
- Additives
- Confinement

Selection of reversible storage material with >80 kg H_2/m^3 / >8 wt.% capacity

Routes for cost effective materials synthesis

- use of waste alloys (e.g. Mg alloy chips from turning)
- less pure raw materials (85 – 95 % purity)
- synthesis from the elements

Development and testing of a boron hydride based hydrogen store

- materials capacity more than 8 wt.% and 80 kg H_2/m^3
- integrated with a Solid Oxide Fuel Cell (SOFC)

Work in the project

WP1: Materials Synthesis (green promising, red less or non promising)

- Pure boron hydride based storage materials (AU, IFE, Empa)
  - porous γ-$Mg(BH_4)_2$, α–$Ca(BH_4)_2$ (AU)
  - $Y(BH_4)_3$, $Mn(BH_4)_2$, $MSc(BH_4)_4$, M = Li, Na, K (AU)
  - unstable boron hydrides, i.e. $Al(BH_4)_3$ and $Zr(BH_4)_4$ (AU, Empa)
  - $Ti(BH_4)_3$ (Empa)
- Boron hydride based composite storage materials (AU, HZG)
  - composites containing two or three stable metal boron hydrides => EMC (LiCa! LiMg => scaffolding), (AU)
  - e.g. MBH_4-$Mg(BH_4)_2$, MBH_4-$Mn(BH_4)_2$ and MBH_4-Mg_{1-x}-$Mnx(BH_4)_2$, M = Li, Na, K
  - less stable boron hydrides, e.g. $Al(BH_4)_3$ and $Zr(BH_4)_4$, plus stable metal boron hydrides, e.g. $LiBH_4$-$Al(BH_4)_3$ or $NaBH_4$-$Zr(BH_4)_4$
- Modified composite boron hydrides (AU, HZG)
  - anion- and/or cation-substituted bi- or tri-metal boron hydrides
  - Reactive composites of boron hydrides, with minor additions of amides/imides (HZG)
  - Li-RHC ($LiH + MgB_2 \Leftrightarrow LiBH_4 + MgH_2$), ~ 10 wt.%, 60 – 100 kg H_2/m^3 for BOR4STORE tank

WP2: Optimisation of Reaction Kinetics

- Transition metal, Co, Cu based halogenised Additives (IFE, HZG)
- Reaction conditions (IFE, HZG)
- Confinement in nanoporous Scaffolds (AU, NCSRD)

WP3: Modelling of Thermodynamics and Kinetics

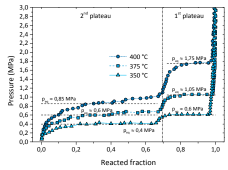
- ab initio structural and dynamic modelling (UNITO)
- Thermodynamic modelling, construction of phase diagrams (UNITO)
- kinetic modelling (UNITO)

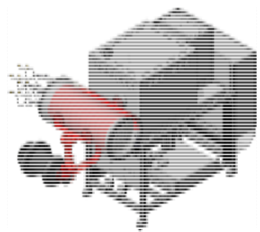
WP4: Routes for Cost Effective Materials Synthesis

- low cost suppliers (ZOZ)
- raw materials with less purity, recycling materials (Katchem, HZG)
- cost analysis of wet chemical and mechano-chemical routes (ZOZ, Katchem, AU, HZG)

WP5: Prototype Construction and Techno-economical Evaluation

- Thermochemical simulation (NCSRD)
- Simulation of heat management (HZG)
- Metal hydride tank construction (ZOZ, HZG, NCSRD)
- System Integration (Abengoa, HZG, ZOZ, NCSRD)
- System Testing (HZG, Abengoa, ZOZ)





Status at End of Project

Status before project	MAIP target	Project Target	Current status/ achievements	Expected future achievements
Capacity of several tons of hydrogen (exact number secret) in metal hydride tanks demonstrated in German FC powered submarines before 2010. Cost > 5000 € / kg of stored hydrogen	Potential for cost below 500 €/kg of stored hydrogen	Capacity 1 kg of hydrogen potential for cost below 500 €/kg = 5 M€/t	Materials cost ca. 3,500 – 7,500 €/kg of stored hydrogen Tank system prototype under construction	Use of recycling alloys, waste (demonstrated on laboratory level) Route for synthesis from elements (demonstrated on laboratory level)
50 g of storage material, > 80 kg H_2/m^3 > 8 wt.% Cycling stability unknown	Storage materials with capacities ≥ 6 wt.%, ≥ 60 kg H_2/m^3	capacities > 80 kg H_2/m^3 and > 8 wt.% Loss of capacity <10% over 500 loading cycles	Ca. 100 kg H_2/m^3 9 – 10 wt.% on materials basis < 7% capacity decrease after 1000 cycles (extrapolated in lab sample)	10 kg of storage material with same capacity, < 5% capacity decrease for 500 cycles in tank

Status before project	AIP target	Project Target	Current status/ achievements	Expected future achievements
Release temperature of boron hydrides >350°C	reversibly releasing hydrogen at operating temperatures compatible e.g. with PEM FC, HT PEM FC or SOFC / MCFC	Release temperature ≤ 450°C (compatible with SOFC)	Release temperatures depending on compound 250 – 450°C	Suitable for operation with SOFC!
Loading time >> 1 h	appropriate hydrogen loading and unloading kinetics for the envisaged application	Loading time < 1 h	Loading time < 1 h in materials testing, loading time of storage tank tbd.	Loading time < 1 h in storage tank (under construction)
Intermetallic hydride based storage systems >40 kg H_2/m^3 < 2 wt.%	Small scale prototype storage systems with significantly improved storage capacity compared to compressed gas storage (≥ 40 kg H_2/m^3, ≥ 4 wt.%,)	Capacity > 40 kg H_2/m^3 > 4 wt.%	Storage system under construction and certification Safe design for high temperature operation ≠ High System capacity	tbd.

Outlook and Prospects

Most promising boron hydride based materials

- Li-RHC, $Mg(BH_4)_2$, EMC in scaffolds, $(Mn(BH_4)_2$

Future materials development targets

- investigation and optimisation of materials cycling stability
- synthesis from low cost raw materials (waste, elements) on industrial scale

Future tank development targets

- proof of functionality (2015/2016)
- design optimisation for lowered cost (amount and kind of steels used, route for manufacturing ⇔ temperature and pressure of operation, safety)

Prospects for Industrial Partners

- Synthesis of Boron hydride based materials, labelled compounds (Katchem)
- Synthesis of Li-RHC on industrial scale (ZOZ)
- Manufacturing of high energy mills, suitable for processing of oxygen and moisture sensitive compounds under protected atmosphere (ZOZ)
- Integration of low pressure, high temperature metal hydride based stores in high temperature cell based applications (Abengoa)
  - SOFC based power supplies with hydrogen as feed gas
  - SOFC / SOEC based Power-2-Power systems

http://www.bor4store.eu • Coordinator contact: klaus.taube@hzg.de
Helmholtz-Zentrum Geesthacht • Max-Planck-Strasse 1 • 21502 Geesthacht • Germany • Phone +49 4152 87 2541• hydrogen.hzg.de
Financial support by the European Fuel Cells and Hydrogen Joint Undertaking (http://www.fch-ju.eu) under collaborative project "BOR4STORE" (Grant agreement no.: N° 303428) is thankfully acknowledged.