TU Clausthal

Clausthal University of Technology

Dehydrogenation of the hydrogen storage material sodium borohydride

M.Szafarska[1,2], G.Sourkouni-Argirusi[1,2], W.Maus-Friedrichs[1,2]

1 Clausthaler Zentrum für Materialtechnik, TU Clausthal, Leibnizstr. 9, 38678 Clausthal–Zellerfeld, Germany

2 Institut für Energieforschung und Physikalische Technologien, Technische Universität Clausthal, Leibnizstr. 4, 38678 Clausthal– Zellerfeld, Germany

Background

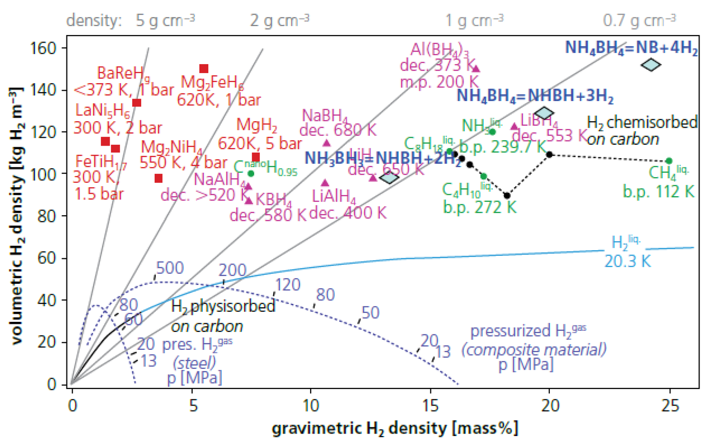
In the last decade, sodium borohydride ($NaBH_4$) has attracted attention in energy storage research, caused by its high hydrogen density of 10.6 wt.% and relatively low cost, making it a potentially better hydrogen (and energy) storage unit compared to compressed hydrogen gas tanks and liquid hydrogen. Therefore it would be an improvement for fuel cell economy and energy storage.

To accomplish this, $NaBH_4$ has to be stabilized against decomposition through reaction with water in humid atmospheres and the dehydrogenation process must be understood properly, especially regarding $NaBH_4$ decomposition during dehydrogenation.
To investigate the dehydrogenation process and the desorbed components of the material, Thermogravimetric- and Multi Gas-Analysis were performed.

The experimental results show correlations between particle size of the material and the desorption rate of hydrogen. In addition, a semi permeable membrane was used to successfully stabilize the $NaBH_4$ against decomposition and analyzed for its influence on the hydrogen desorption process.

Solid hydrogen storage materials

- **Advantages** vs. common Hydrogen storing techniques:
  - Theoretically higher gravimetric and volumetric hydrogen density
    - Consequence: Higher energy storage potential
  - Higher safety
  - Better transportability
- **Disadvantages**:
  - High material costs up to this date
  - Rehydration processes have do be developed
  - Lifetime short if in direct contact with air

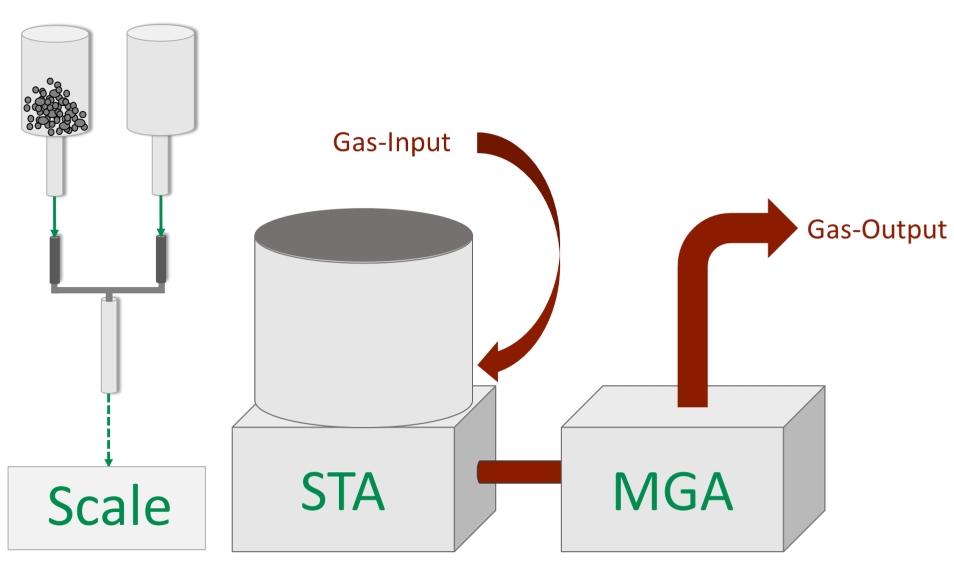


Source: Sigma-Aldrich Bulletin „*Hydrogen Storage Materials*", **2007**, VOL. 2 N. 2

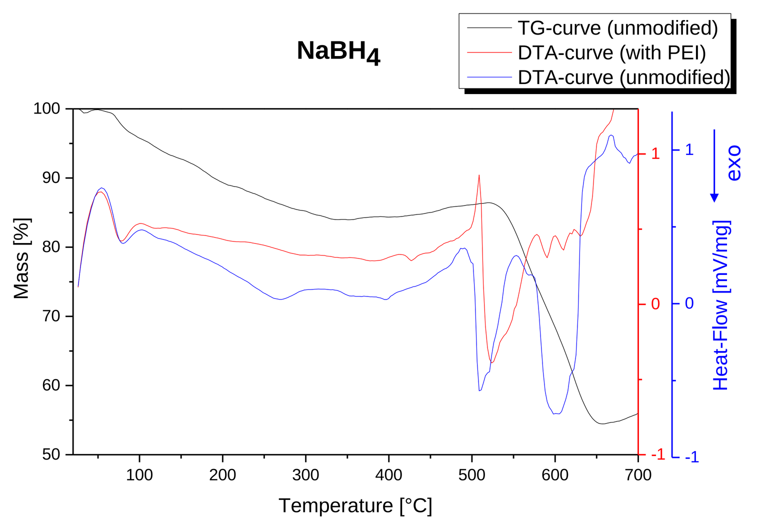
Type	Costs (USD/g)	H_2 density (wt%)	T_d (°C)	Reaction
$NaBH_4$	6,47	10,6	505	$NaBH_4 \rightarrow Na + B + 2H_2$
$LiBH_4$	15,65	18,5	380	$LiBH_4 \rightarrow Li + B + 2H_2$
$Mg(BH_4)_2$	116,5	14,9	320	$Mg(BH_4)_2 \rightarrow MgB_2 + 4H_2$
$Ca(BH_4)_2$	142	11,6	367	$Ca(BH_4)_2 \rightarrow 2/3CaH_2 + 1/3CaB_6 + 10/3H_2$

Comparion of several Borohydrides

TGA & DTA/DSC Measurements



Setup of the experiment



- **Quantitatively** measurements of uncoated and coated NaBH4 via TGA and DTA/DSC
- **Qualitatively** measurements of desorbed components via MGT and MGA

- The TGA curve shows two steps in which mass was lost:
  - Step 1: ~ 100°C – 350°C (Water)
  - Step 2: ~ 500°C – 650°C (Hydrogen)

- The DTA curves show significant differences regarding the exothermic phase transitions:
  - Starting at 500°C and 550°C for the unmodified sample
  - and only one at 500°C for the modified sample

Discussion

While the unmodified sodiumborohydride shows two exothermic phase transition peaks in the DTA-curve, the second peak at 600°C is significantly smaller in the modified substance. This may be caused by the observed synergy effect of the PEI coating [1].

The mass spectrum delivered by the MGT measurement of $NaBH_4$ in a UHV suggests that the hydrogen desorption process initiates at about 175°C under low pressure conditions.

The mass spectrum delivered by the simultaneous MGA measurement confirms that the hydrogen desorption process starts around 500°C at atmospheric pressure.

During both pressure conditions, water seems to be the only component that has a smaller desorption temperature than hydrogen does.

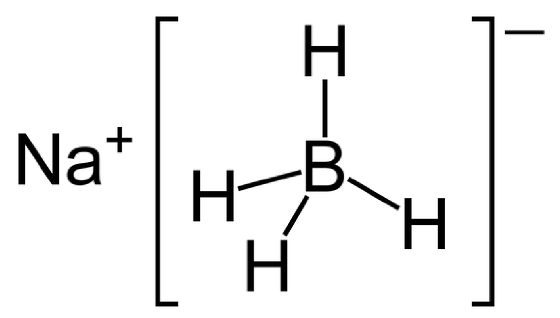
Experimental

Thermogravimetric Analysis/TGA: Ar-Atmosphere, 5K/min, 293K – 973K
Multi-Gas-Analysis/MGA: pressure during measurement: $\sim 5 \cdot 10^{-6}$ mBar
Multi-Gas-Analysis with thermic desorption/MGT: pressure during measurement: $\sim 1 \cdot 10^{-7}$ mBar

Sodiumborohydride/NaBH4 from Sigma-Aldrich ®
Polyethylenimine/PEI from Sigma-Aldrich ®

The Sodiumborohydride was heated from room temperature to 700° C and the corresponding TGA and DTA curves measured. Meanwhile the desorbed gas-components were qualitatively analyzed via MGA measurements.

NaBH4

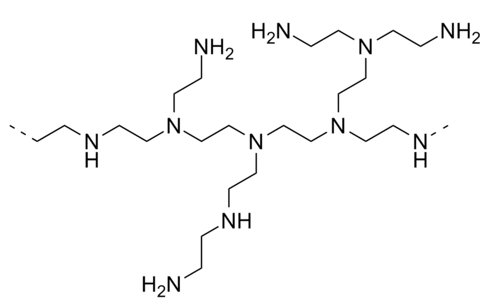


Lewis Structure of NaBH4

Storing method	Storing-Specification	Volumetric storing capacity
$NaBH_4$	solid	~ 150 g H_2/L
$NaBH_4$	30 wt% solution	63 g H_2/L
liquid H_2	cryogenically-cooled (-259°C)	71g H_2/L
pressurized H_2	~ 300 bar	23g H_2/L
	~ 600 bar	39g H_2/L

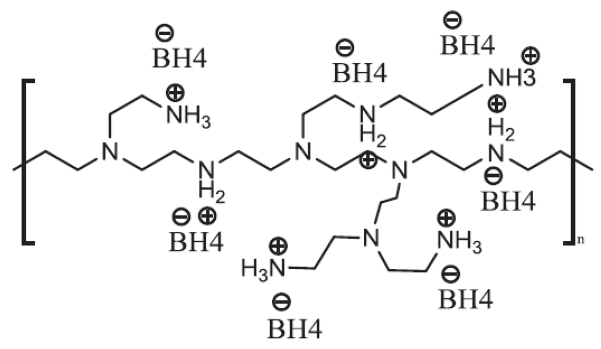
Comparison of several hydrogen storing methods

- **Pros**:
  - Relatively low costs
  - High Hydrogen density of 10,6 wt%
  - High lifetime when isolated from air
- **Cons**:
  - Relatively high desorption temperature
  - Unsolved rehydration mechanism
  - Synthetization process could still be optimized
- **Modification with Polyethylenimine (PEI)**:
  - Stabilization against decomposition
  - in humid atmospheres



Structure of Polyethylenimine

Coating of NaBH4 with Polyethylenimine

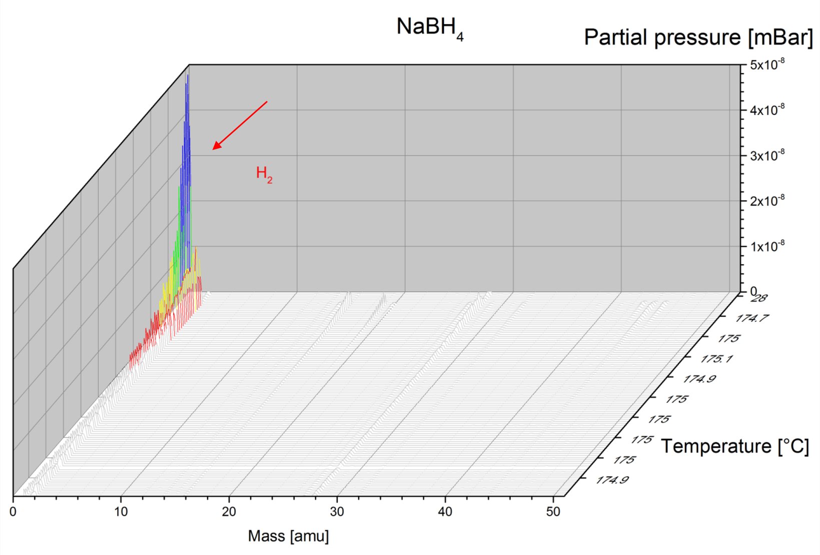


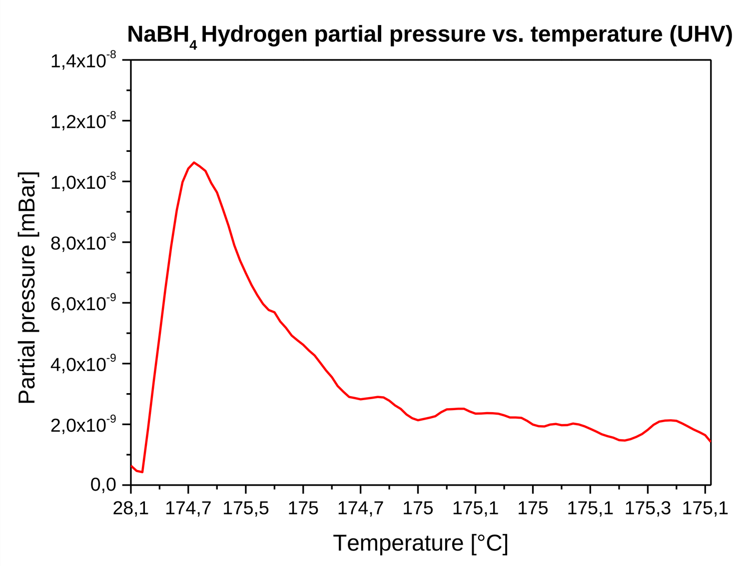
Suggested structuce by [2] of NaBH4 coated with polyethylenimine

MGA & MGT Measurements

In UHV conditions:

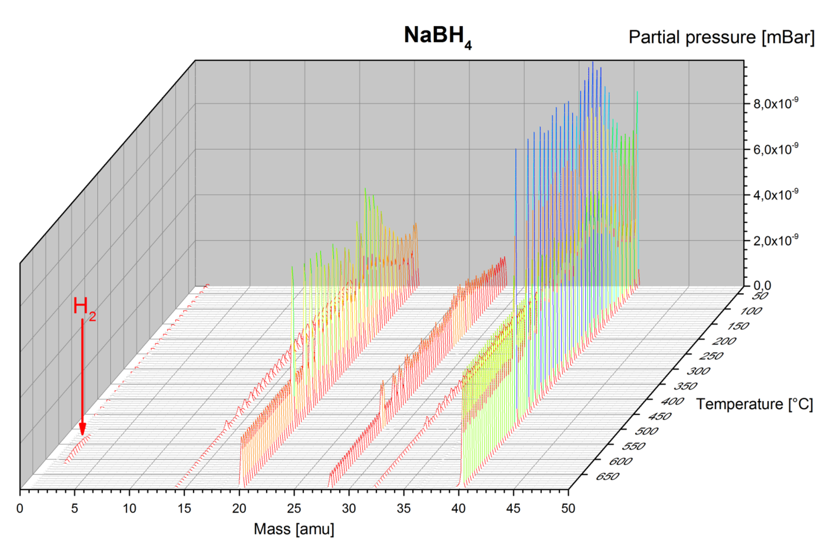
- $NaBH_4$ was heated until the hydrogen desorption process started (at 175°C). Then, temperature was held constant.

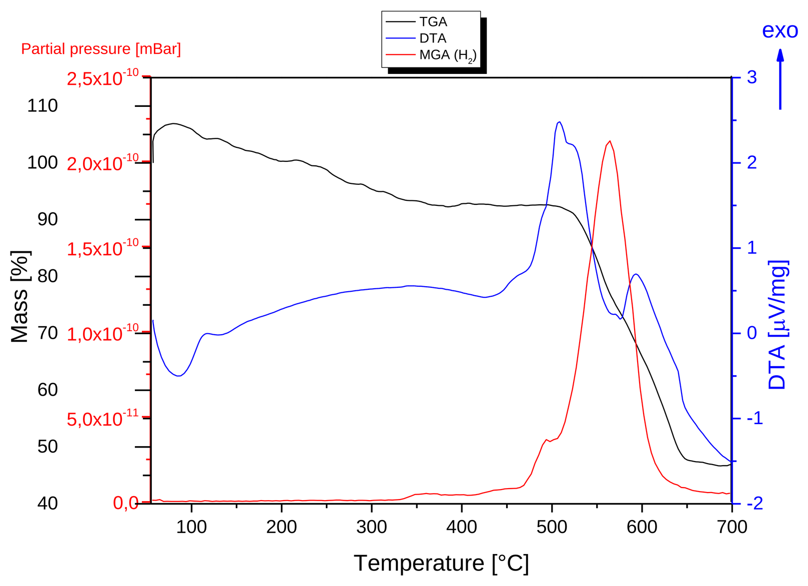




In normal atmospheric pressure conditions:

- Sample heated from 25°C – 700°C with a heating speed of 5K / min.





Summary

The TGA measurements show no significant difference between modified and unmodified sodiumborohydride regarding desorption temperatures or amount of desorbed components.

The DTA/DSC curves show that the modification with PEI almost eliminates the second phase transition, which can be caused by the observed synergy effect in Literature [1].

The MGT/MGA measurements show, that hydrogen starts to desorb at about 175°C in UHV conditions and at around 500°C under atmospheric pressure.

All in all the combination of Thermogravimetric analysis and mass spectrometry is a useful tool to analyse the desorption of hydrogen from sodiumborohydride not only quantitatively but also qualitatively.

[1] Dahle S, et al., RSC Adv., 2014, **4**, 2628
[2] Sourkouni G, et al., Interaction mechanism of hydrogen storage materials with layer-by-layer applied protective polyelectrolyte coatings, International Journal of Hydrogen Energy (2014)

maik.szafarska@tu-clausthal.de

http://www.czm.tu-clausthal.de