BOR4STORE Report Summary

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Final Report Summary - BOR4STORE (Fast, reliable and cost effective boron hydride based high capacity solid state hydrogen storage materials)

Executive Summary:
BOR4STORE was a collaborative project, funded by the FCH JU between 2012 and 2015. 3 industrial companies, thereof two SMEs, and 6 European research institutes investigated the use of boron hydride based materials for stationary hydrogen storage with a focus on supply of high temperature fuel cells like SOFCs.
BOR4STORE started with a broad range of boron hydride based materials, promising very high hydrogen storage capacities between 8 and up to 18 wt.%, though for many of them at the expense of comparably high reaction temperatures up to nearly 500°C. They ranged from single cation materials (e.g. Ca(BH4)2, Mg(BH4)2 or novel Mn(BH4)2 and Y(BH4)3) over composites of different boron hydrides (e.g. the eutectically melting composite (EMC) LiBH4 – Ca(BH4)2) or with other hydrides (e.g. the Reactive Hydride Composite (RHC) LiBH4-MgH2) to composites, infiltrated into various nanoporous materials. Furthermore, materials tending to decompose spontaneously already at room temperature (like Al(BH4)3 and Zr(BH4)4), were investigated.
All materials underwent a basic characterisation of their hydrogenation properties and microstructure. Based on a multicriteria based downselection scheme (capacity, reaction heat, cycling properties etc.), selected materials were investigated more deeply, and their reaction schemes investigated e.g. by advanced IR, synchrotron and NMR techniques, and conclusions on how to influence reaction steps limiting reaction rates were drawn. Several additives as well as confinement into nanoporous structures were investigated with a focus on enhancing reaction speeds and cycling stability.
All these experiments were accompanied by theoretical modelling activities. The exchange of data with the models lead to verification of the models, vice versa e.g. theoretical calculations of IR and NMR spectra lead to a deeper understanding of features found in these experimental data.
Summarising, it can be said, that nearly all mono boron hydride materials are difficult to rehydrogenate from the gas phase, and show a strong decrease of hydrogen storage capacity during the first reloading cycles. Partially, this is due to the tendency to release diborane instead of pure hydrogen with boron hydrides decomposing below 200°C. Unstable boron hydrides were found practically not be handable for hydrogen storage. Mg(BH4)2 showed a reversibility of a few wt.% at temperatures below 300°C. EMCs exhibited significantly higher reversible hydrogen release, though a significant drop of ca. 40 - 60% of their storage capacity in the first cycle. Together with their intended use, i.e. infiltrated in nanoporous scaffolds at degrees of pore filling around 60%, this lead to reversible storage capacities of 4 – 6 wt.%. Concluding, the most promising boron hydride based materials were the RHCs, namely the LiBH4-MgH2, some EMC (e.g. LiBH4-Ca(BH4)2) and Mg(BH4)2.
BOR4STORE strived also for the development of cost effective routes for synthesis of the hydrogen storage materials. Various wet chemical as well as mechano-chemical routes and combinations were analysed with respect for their potential for yielding cost effective hydrogen storage materials. It was found, that besides the raw materials themselves, especially all the wet chemical reaction steps were associated with rather high cost for e.g. solvents, long reaction times and necessary purification of the synthesised compounds, whereas in dry mechano-chemical processing effectively 100% of the educt materials could be converted to the desired products in a very short time. It was estimated, that mechano-chemical processing by high energy milling should add less than 2 €/kg of processed materials in large scale processing. These cost have to be compared with cost for educt materials between at minimum 10 – 20 €/kg, but today often significantly higher and more than 100 €/kg. It was found, that the cost for boron hydride based hydrogen storage materials range from currently a minimum of ca. 3.500 €/kg of stored hydrogen to 8.000 and more. This is partially due to the more or less lab scale status of boron hydride synthesis. A decrease of cost of a factor 5 to 10 could be expected, if industrial scale facilities for materials synthesis would be established. Further cost decreases of 50% by using recycled raw materials (e.g. metal scrap, which cannot be used elsewhere), lower purity raw materials and reconsidering the production routes, starting from the ores and elements, can be expected.
The LiBH4-MgH2 RHC, together with a suitable and cost effective additive, was selected for constructing a prototype hydrogen storage module, containing 500 g of the storage materials and storing ca. 50 g H2. Due to significant delays in the construction, building and TÜV certification as a pressurised container, it was not possible to perform any testing of this prototype tank module within the project time frame.
Theoretical estimates of the achievable system capacity of boron hydride based hydrogen storage lead to the conclusion, that even with a storage material of ca. 10 wt.%, at reaction temperatures of ca. 500°C and internal loading

pressures of 50 bar, a maximum of 2 – 3 wt.% and 30 – 40 kg H2/m3 seems feasible. Further significant increases of capacity will be obtained by reducing the temperature of operation and loading pressure.
Due to the non-availability of a tank, the thermal integration of a metal hydride store with the 1,2 kW SOFC, purchased for BOR4STORE, was investigated by various simulation models. These showed, that an optimised thermal heat management system, based on transferring the off-heat of the SOFC from its exhaust gases via a heat exchanger and a heat transfer medium to the hydrogen store, would be suitable for releasing the necessary amount of hydrogen from the hydrogen store for supply of the SOFC. I.e. no extra electric heating should be necessary.

Project Context and Objectives:
c.f. file "BOR4STORE_303428_Final-Report.pdf"

Project Results:
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Potential Impact:
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Related information

Documents and Publications	final1-bor4store-303428-final-report.pdf final1-bor4store-303428-images.pdf

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