

THE IMPACT OF NANOPOROUS CARBON ON THE HYDROGEN STORAGE PROPERTIES OF LIGHT METAL HYDRIDES

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Introduction

Light metal hydrides are candidates for compact and efficient reversible on-board hydrogen storage. However, at the moment no known material fulfills all requirements regarding hydrogen content, release temperature, and reversibility simultaneously. Binary light metal hydrides generally are thermodynamically too stable, while in addition boronhydrides, alanates and other complex systems contain multiple phases upon dehydrogenation, causing reversibility issues due to phase segregation.

A general approach to the preparation of hydrogen storage materials is high energy ball milling, which decreases the crystallite size and allows the addition of catalysts. In an alternative approach, we study the effect of nanosizing the metal hydrides (<10 nm), and supporting or confining them in a porous matrix. This is not only expected to improve the kinetics, but can potentially also change the thermodynamics of the systems [1-3]. Furthermore, nanoconfinement can benefit the reversibility by limiting macroscopic phase segregation upon cycling [4], while the addition of carbon can also lead to better mechanical stability and thermal management. On the other hand the addition of a support or scaffold compromises the overall gravimetric hydrogen content of the material system.

We investigate the effect of nanosizing light metal hydrides and supporting them on nanoporous carbon by melt infiltration. We demonstrated the impact on hydrogen sorption properties for several hydrides (NaAlH_4 , NaH , LiBH_4 and MgH_2) [5-9].

Experimental

Nanoconfined materials were prepared by solution impregnation and/or melt infiltration of nanoporous carbon or silica matrices. For details we refer to the relevant publications [5-9]. For instance for Mg the carbon support was dried and then physically mixed with MgH_2 . The mixture was then first heated to above the decomposition temperature of MgH_2 to in situ generate Mg metal, and then further heated under inert atmosphere up to the melting point of Mg, leading to spontaneous infiltration of the porous matrix by molten Mg. Cooling down was performed under H_2 atmosphere. The steps in this process are illustrated in Figure 1 [7].

The complex metal hydrides (such as NaAlH_4 and LiBH_4) were melt-infiltrated under high hydrogen pressures, to

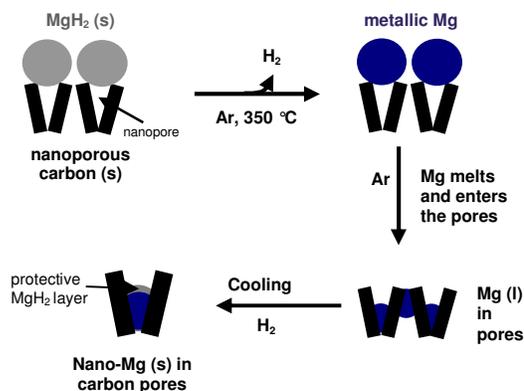


Fig. 1 Schematic representation of the process to form a Mg/C nanocomposite starting from MgH_2 and nanoporous carbon.

prevent decomposition of the complex metal hydride during melting. Small amounts of catalysts, such as Ni, were deposited onto the carbon by solution impregnation and heat treatments, prior to the melt infiltration.

Structural characterisation was based on N_2 physisorption, XRD, solid state NMR, EXAFS and electron microscopy. The impact of the nanosizing and confinement on the hydrogen sorption properties was investigated by both gravimetric (Rubotherm) and manometric (Setaram PCT-Pro) H_2 sorption measurements, as well as temperature-programmed H_2 desorption measurements using a TCD detector.

Results and discussion

N_2 physisorption was one of the techniques used to investigate the melt infiltration process. As an example figure 2 displays the differential pore volume as a function of pore size upon melt infiltration of nanoporous carbon with different loadings of NaAlH_4 .

With increasing loading the remaining pore volume of the carbon decreases, while upon leaching the NaAlH_4 the original pore volume of the carbon is restored. This suggests that the NaAlH_4 is confined in the pores. This was further confirmed by XRD measurements and solid state NMR. Also for LiBH_4 ,

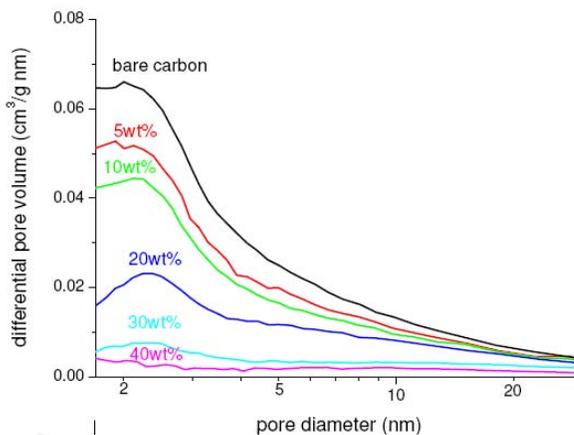


Fig. 2 Differential pore volume of nanoporous carbon upon melt infiltration with different loadings of NaAlH_4 as indicated. [7]

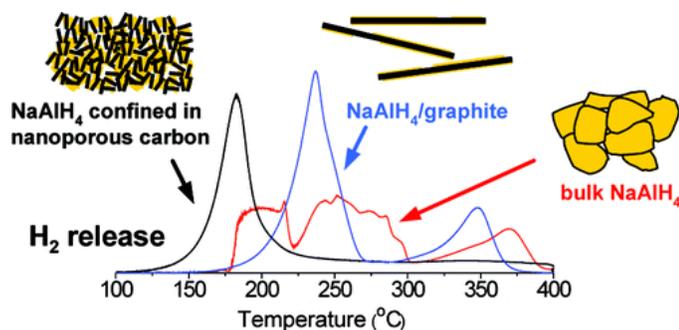


Fig. 3 H₂ desorption from NaAlH₄ in nanocomposites based on nanoporous carbon and non-porous high surface area graphite, and as a reference bulk NaAlH₄ without carbon additives. Hydrogen desorption was measured in Ar flow, heating with 5 °C/min.

NaH and Mg(Ni)H₂ it was shown that high loadings of the active materials could be confined in the porous matrices, which generally resulted in non-crystalline material.

The confinement of the active material in a nanoporous carbon or silica matrix had a pronounced influence on the hydrogen desorption properties for all materials that we investigated. As an example in Figure 3 we show the hydrogen release properties for NaAlH₄, comparing a bulk material, NaAlH₄ molten in the presence of non-porous high surface area graphite, and NaAlH₄ confined in a nanoporous carbon. The presence of the carbon has a large impact on the hydrogen desorption, leading to a single release peak instead of the three separate steps typically observed for (catalyzed) bulk NaAlH₄. Furthermore the rehydrogenation efficiency under mild conditions (for instance 24 bar and 150 °C) had significantly increased. Remarkably we found that the nanoconfinement had also changed the decomposition pathway, and led to a shift in the thermodynamics of the equilibrium $3\text{NaAlH}_4 \leftrightarrow \text{Na}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2$. [5]

Particularly interesting is also the last decomposition step, $2\text{NaH} \leftrightarrow 2\text{Na} + \text{H}_2$, which is not visible as a separate step for the nanoconfined material. To investigate this step in detail, we studied NaH/C nanocomposites with various loadings. Figure

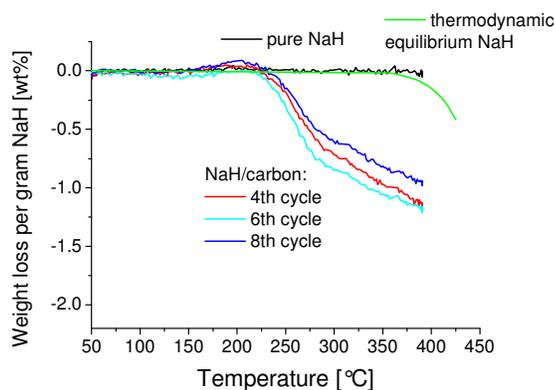


Fig. 4 Gravimetric measurement of the repeated dehydrogenation of 33 wt% NaH/porous carbon measured under 1 bar H₂ flow. Indicated is also the onset temperature at which thermodynamically bulk NaH would be expected to start decomposing under 1 bar H₂ pressure.

4 shows the cycling of a 33 wt% NaH/carbon nanocomposite under 1 bar H₂ pressure. We found that not only the kinetics were clearly enhanced (for instance allowing partial reloading of the NaH/C system at 1 bar H₂ pressure and room temperature), but also under 1 bar pressure some H₂ is released 200 °C below the equilibrium decomposition temperature of bulk NaH. [9]

Conclusions

Light metal hydrides can effectively be confined in nanoporous matrices by the melt infiltration process. The onfinement in the nanopores (<10 nm) has a large impact on the hydrogen sorption properties, not only on the kinetics, but also on the reversibility and even on the thermodynamics.

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