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 borohydrides, 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 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. 1 Schematic representation of the process to form a Mg/C nanocomposite starting from MgH$_2$ and nanoporous carbon.

Fig. 2 Differential pore volume of nanoporous carbon upon melt infiltration with different loadings of NaAlH$_4$ as indicated. [7]
NaH and Mg(Ni)H$_2$ 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 NaAlH$_4$, comparing a bulk material, NaAlH$_4$ molten in the presence of non-porous high surface area graphite, and NaAlH$_4$ 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 NaAlH$_4$. 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 $3\text{NaAlH}_4\rightarrow \text{Na}_3\text{AlH}_6+2\text{Al}+3\text{H}_2$. [5]

Particularly interesting is also the last decomposition step, $2\text{NaH} \rightarrow 2\text{Na}+\text{H}_2$, 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 4 shows the cycling of a 33 wt% NaH/carbon nanocomposite under 1 bar H$_2$ pressure. We found that not only the kinetics were clearly enhanced (for instance allowing partial reloading of the NaH/C system at 1 bar H$_2$ pressure and room temperature), but also under 1 bar pressure some H$_2$ 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 confinement 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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**References**