Nanosized (complex) metal hydrides for hydrogen storage prepared by melt infiltration of porous carbon materials

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Introduction

Metal hydrides are promising materials for the future on-board storage of hydrogen, as they allow the storage of large quantities of hydrogen in a small volume at room temperature. Uptake and release of hydrogen can be controlled by altering temperature and pressure (*metal hydride* <---> *metal* + H_2). However, most of the metal hydrides are thermodynamically too stable and release hydrogen at temperatures that are too high for practical applications. Furthermore, kinetics are often slow leading to hydrogen release/uptake at insufficient rates and often poor reversibility. A promising approach to improve kinetics and possibly to alter the thermodynamics of a metal (hydride) system is to reduce the particle size to the nanometer scale. In this size regime, diffusion limitation is minimized and even changes in the thermodynamic properties of the metal (hydride) can be expected [1]. One route to synthesize nanosized particles is to deposit the desired compound onto a porous support. Recently it was shown that significant improvements in terms of kinetics and reversibility can be obtained this way by depositing e.g. ammonia borane [2] and $LiBH_4$ [3] in porous silica and carbon materials.

In this project, we synthesize nanosized (complex) metal hydrides by novel melt infiltration techniques using nanoporous carbons as support. We study how kinetics and thermodynamics of the (de)hydrogenation reaction can be influenced by particle size and interaction with the carbon matrix. We discuss MgH_2 (7.7 wt% H), $Mg_xNi_yH_z$, $NaAlH_4$ (7.4 wt%), NaH, (4.2wt%), and LiH (12.7 wt%).

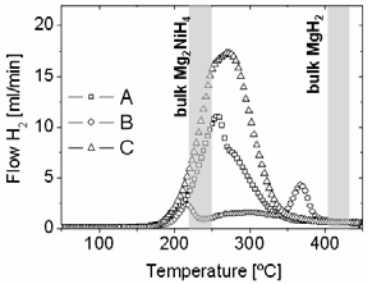
Materials and Methods

Nanosized Mg is synthesized using melt infiltration as described in an earlier work [4]. To obtain Mg_xNi_y samples, Ni is predeposited onto the carbon support. Hydrogenation is conducted in an autoclave at 325 ºC (under 100 bar H_2 pressure for Mg and 50 bar for Mg_xNi_y) For the other hydrides, a modified melt infiltration process is used. The weight fraction of metal hydride on carbon is typically between 10-70 %. The composite materials are characterized by XRD, nitrogen physisorption, SEM and TEM. Hydrogen sorption properties are investigated using thermally programmed desorption (TPD), gravimetric and volumetric measurement techniques.

Results and Discussion

We find that the hydrogen storage properties of the synthesized nanocomposite materials are significantly improved compared to the bulk hydrides. As an example, the first hydrogen desorption of $Mg_xNi_yH_z$/carbon nanocomposites is shown in Figure 1. Hydrogen release at lower temperatures is expected in the case of Mg_2NiH_4 formation, however the samples shown here exhibit much higher Mg:Ni ratios. Compared to bulk MgH_2 a significant shift towards lower temperatures is found for all samples. It can be seen that the desorption profile is strongly influenced by the Mg:Ni atomic ratio and the carbon content. Sample B shows two distinct release temperatures that could be attributed to nanosized Mg_2NiH_4 and MgH_2. Additionally, a broad intermediate step is found. An increase in the MgH_2 loading surprisingly leads the disappearance of the clear signature for MgH_2 and Mg_2NiH_4 phases (sample C). A similar behavior is found for the sample with a more intermediate composition (sample A). Structural characterization and hydrogen desorption properties indicate that an intimate mixing of magnesium, nickel and carbon on a nanoscale occurs during melt infiltration, leading to hydrogen desorption temperatures which can be tuned by the stoichiometry of the sample. The samples show storage efficiencies as high as 85%.

We also find that the particle size is influenced by the nature of the carbon. For example, Mg nanoparticles around ~2 nm in diameter can be synthesized by choosing microporous carbon as support. Accordingly, larger particles are found for carbon supports also exhibiting mesopores. Preliminary results on the hydrogen storage properties show that the hydrogen desorption process of melt infiltrated metal hydrides can be strongly influenced by the nature of the carbon support.



	Mg : Ni atomic ratio	Carbon content wt%	wt% H_2 expected	wt% H_2 obtained
A	8	68	1.15	0.65
B	15	83	1.91	1.57
C	17	45	3.83	2.71

Figure 1. Hydrogen desorption profiles for $Mg_xNi_yH_z$/carbon nanocomposites (Thermal programmed desorption under Ar atmosphere (25 ml/min) at a heating rate of 5 K*min^{-1})

Significance

The present work shows that melt infiltration of porous carbons is an effective way to synthesize nanosized metal (hydrides) and significant improvements of the hydrogen storage properties are obtained. The carbon support additionally contributes to a better thermal conductivity of the overall system, rendering the possibility of improved thermal management to steer the large heat flows that occur during reaction.

References

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