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Reversibility of the hydrogen desorption from LiBH₄: a synergetic effect of nanoconfinement and Ni addition†‡

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The reversible hydrogen capacity of LiBH₄ was improved by a combination of Ni addition, nanosizing and confinement of the active phase in a nanoporous carbon scaffold.
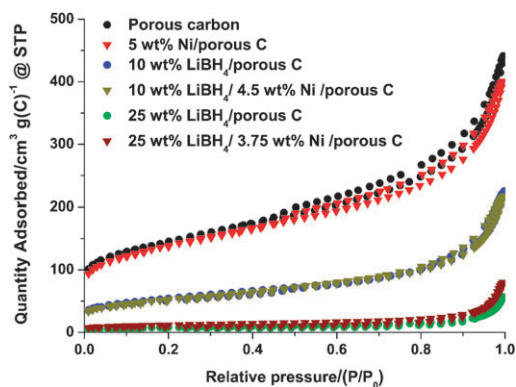
An effective hydrogen storage system is one of the most challenging technical issues facing the use of hydrogen as a fuel for cars.[1] Hydrogen can be stored in gaseous or liquid form but none of these methods satisfies all requirements for mobile applications. Storage in gaseous form requires compression to high pressures (up to 800 bar), and safety, gas tank weight and volume are important issues. Liquid storage involves cooling to low temperatures ($-253\ °C$), which implies large energy losses. Solid state hydrogen storage in metal hydrides is advantageous especially in terms of safety and effective volumetric hydrogen content. For example, lithium borohydride (LiBH₄) contains 18.5 wt% hydrogen. However, it is thermodynamically stable, and requires heating to above 400 °C to release the hydrogen. Furthermore, it shows slow de/rehydrogenation kinetics, with 8.3 wt% H₂ reabsorbed only after charging at 600 °C and 155 bar for 200 min.[2,3]

A large effort has been devoted to identify an effective catalyst for (de)hydrogenation of LiBH₄. This includes the use of metal oxides and halides, Pt, Ni, and carbon nano-materials.[4–10] Although addition of these materials resulted in lower dehydrogenation temperatures, there was no large impact on reversibility. For example, ball milling LiBH₄ with Ni decreased the onset of hydrogen release to 300 °C, but severe conditions (600 °C, 100 bar H₂ for 30 h) were still required for partial rehydrogenation (12 wt% H₂) of the system. A recent promising strategy to improve the H₂ sorption kinetics of metal hydrides is nanoconfinement in porous materials. For instance LiBH₄ incorporated into a carbon scaffold shows faster dehydrogenation and rehydrogenation than bulk LiBH₄.[11] Furthermore, nanoconfinement can even alter the thermodynamical stability of metal hydrides as has been demonstrated for NaAlH₄.[12,13] Here we report a large enhancement of the reversibility of hydrogen sorption in LiBH₄ by a synergetic effect of nanoconfinement and Ni addition.

Ni/LiBH₄/C nanocomposites were synthesized by impregnation of high surface area porous carbon (HSAG-500,

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Timcal Ltd., pore volume 0.66 cm³ g⁻¹, BET surface area 500 m² g⁻¹, broad pore size distribution dominated by 2–3 nm pores) with nickel citrate solution, followed by melt infiltration with LiBH₄ (for experimental details see ESI‡). A convenient method to follow the pore filling upon melt infiltration is N₂ physisorption (Fig. 1). The porosity of the carbon decreased steadily with increasing LiBH₄ loading. 84% of the pore volume was filled for a nanocomposite containing 25 wt% LiBH₄ while the observed pore volume was nil for nano-composites containing more than 30 wt% LiBH₄. This is in good agreement with the amount of LiBH₄ (31 wt%) expected to be required for a complete filling of the carbon pores. Carbon has a low surface energy, and Ni has been used as an effective wetting agent for melt infiltration of carbon with Mg.[14,15] However, the wetting of carbon with molten LiBH₄ does not seem critical, and no difference is seen in the pore volume filled with and without Ni.

Ni is a classical (de)hydrogenation catalyst, and hence we were interested in its influence on the hydrogen desorption from LiBH₄. Fig. 2A illustrates the hydrogen release of nanocomposites of 25 wt% LiBH₄ in porous carbon, without Ni and with 3.75 wt% Ni. For a comparison we also show 25 wt% LiBH₄ melted under the same conditions but with non-porous graphite (BET surface area 7 m² g⁻¹). The LiBH₄/graphite sample exhibits minor H₂ desorption around 280 °C (the melting of LiBH₄), and a major desorption peak around 430 °C, which is lower than for bulk LiBH₄ (500 °C).[2,3] For the nanoconfined LiBH₄, H₂ release started already at 200 °C with a maximum desorption rate at 350 °C. For the sample to which Ni has been added, the onset of hydrogen release is even lower, but the difference is small. All samples release about 3.5 wt% H₂ per g sample or 14 wt% H₂ per g LiBH₄ (for the nanoconfined samples dwelling
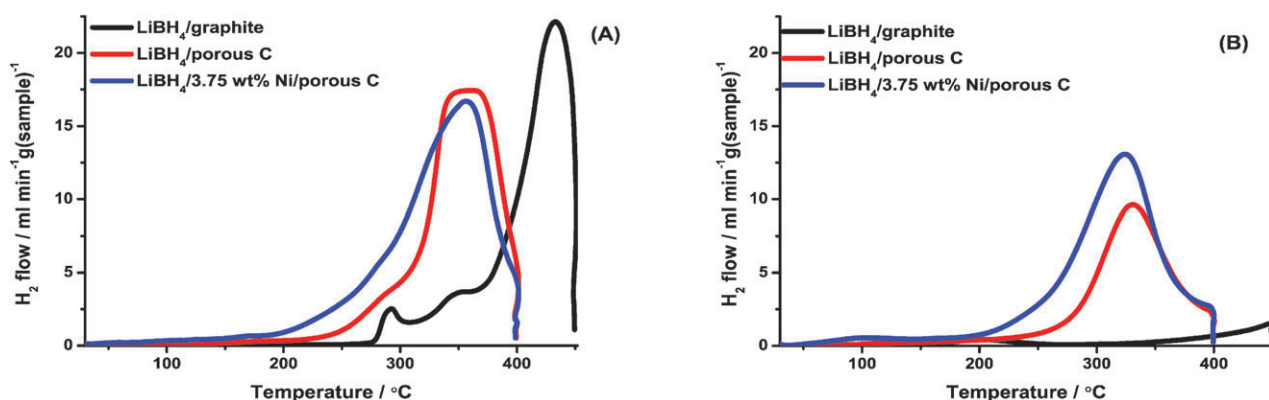

Fig. 1 N₂-physisorption results for different LiBH₄(Ni)/carbon nanocomposites, showing the gradual loss of carbon porosity with increasing LiBH₄ loading.

Fig. 2 H_2 release while heating the samples with 5 °C min^{-1} in Ar flow (A) first desorption—after synthesis; (B) second desorption—after rehydrogenation of the desorbed samples under 40 bar H_2, at 320 °C for 2 h.

25 min at 400 °C, for the LiBH$_4$/graphite at 450 °C), close to the amount expected for decomposition of LiBH$_4$ to LiH, B and H$_2$. It is clear that nanoconfinement in porous carbon lowers the hydrogen release temperature by ~100 °C compared to the non-confined LiBH$_4$/graphite, as reported in the literature.[11] The presence of Ni had no major impact on the dehydrogenation, which underlines that most likely the association of atomic H$_2$ to form molecular H$_2$ at the surface is not a rate limiting step in the H$_2$ release from LiBH$_4$.

To evaluate the reversibility under mild conditions, the dehydrogenated samples were hydrogenated in an autoclave at 320 °C and 40 bar H$_2$ for 120 min. Fig. 2B shows the hydrogen release of the rehydrogenated samples. The LiBH$_4$/graphite sample released a negligible amount of hydrogen. The LiBH$_4$/porous C nanocomposite released 1.45 wt% (5.8 wt% H$_2$ per LiBH$_4$). Surprisingly, the Ni containing sample released 2.3 wt% (9.2 wt% H$_2$ per LiBH$_4$). This behaviour was reproduced with samples containing only 0.75 wt% Ni.

To further investigate the role of the Ni, we gravimetrically followed the H$_2$ uptake of the nanocomposites after the first desorption, rehydrogenating at 320 °C under 40 bar H$_2$ pressure (Fig. 3). A negligible amount of H$_2$ was absorbed in the sample containing LiBH$_4$ and graphite. The confined
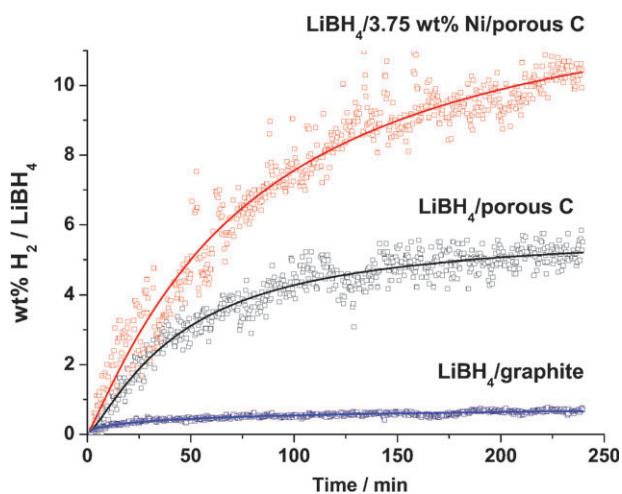
Fig. 3 Hydrogen uptake of LiBH$_4$(Ni)/C nanocomposites measured gravimetrically at 320 °C under 40 bar H$_2$ flow.

LiBH$_4$ without Ni absorbed about 6 wt% H$_2$ (g LiBH$_4$)$^{-1}$ while the Ni containing sample absorbed about 10 wt% H$_2$ (g LiBH$_4$)$^{-1}$, in fair agreement with the amount of H$_2$ released in the second desorption run. It is clear that the uptake of H$_2$ rather than the release is the critical step limiting the reversibility. For the sample without Ni, it seems that the uptake levels off after about 1 h of absorption.

Unfortunately, gravimetric uptake measurements do not accurately reflect the initial uptake kinetics (as ~40 min are needed to reach the designated pressure of 40 bar). Additional manometric ("volumetric") uptake measurements (Fig. S1 and S2, ESI‡) show a very fast initial hydrogen uptake. Hence it seems that a fraction of the material can be hydrogenated very rapidly under mild conditions, while for another part of the sample the H$_2$ uptake is much more sluggish. In the presence of Ni, the amount that can be absorbed in the first 5 minutes is significantly enhanced.

It is interesting to speculate about the origin of the effect of Ni addition. A first guess could be that Ni acts as a hydrogenation catalyst. Before melt infiltration 5–7 nm crystalline Ni nanoparticles located in the carbon pores were detected by transmission electron microscopy and X-ray diffraction, but after addition of the LiBH$_4$ no crystalline Ni-containing species were found. Preliminary results from extended X-ray absorption spectroscopy (EXAFS) indicated that nickel boride (Ni$_x$B) phases were present after melt infiltration, and during subsequent cycling. It is reported in literature that nickel boride can act as a hydrogenation catalyst.[16,17] However, a careful look at the hydrogen uptake indicates that Ni does not simply work as a catalyst enhancing the overall uptake rates. Instead, the addition of Ni enlarged the fraction of the material that was available for rapid rehydrogenation under mild conditions. This suggests that Ni influences the microstructure and phase evolution of the boron phases. For complex metal hydrides, macroscopically segregated phases are often formed after dehydrogenation. Since solid state diffusion needed to enable their recombination upon rehydrogenation is slow, this might play an important role in limiting the reversibility. Hence it might be that due to the formation of Ni$_x$B, boron phases are "pinned" inside the porous scaffold, limiting the macroscopic phase segregation. Another possibility is that Ni$_x$B acts as a nucleation centre for the formation of the LiBH$_4$ phase. Alternatively, Li$_2$B$_{12}$H$_{12}$ has been identified as

an important intermediate in the LiBH$_4$ decomposition and reformation,[18] and it is speculated that the stability of the Li$_2$B$_{12}$H$_{12}$ phase is an important factor in limiting the reversibility of the hydrogen sorption. It could be that the nanoconfinement and presence of Ni species influence the reaction pathway such that the formation and conversion of Li$_2$B$_{12}$H$_{12}$ is affected. Such a change in reaction pathway due to nanoconfinement was previously reported for NaAlH$_4$.[19] A comprehensive study of the evolution of the different phases in the nanocomposites is the topic of present studies and will be discussed elsewhere.

In summary, we have shown that the hydrogen sorption properties of LiBH$_4$ were markedly increased by the synergetic effects of nanoconfinement and Ni addition. Confining LiBH$_4$ in nanoporous carbon resulted in a 100–150 °C decrease in the dehydrogenation temperature compared to bulk LiBH$_4$. The amount of material that could be rehydrogenated rapidly and under mild conditions was further enhanced significantly upon the addition of Ni to the system. These findings are very relevant as reversibility is one of the major challenges facing the use of complex hydrides for hydrogen storage.

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