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Improvements of kinetic properties of $LiBH_4$ by supporting on MSU-H type mesoporous silica

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Lithium borohydride ($LiBH_4$) is a promising material for hydrogen storage, featuring a high gravimetric storage density (above 13 wt. % in the first decomposition step). However, studies of re-hydrogenation of the decomposition products have proven less successful, leading us to the requirement of modified-$LiBH_4$ materials with better absorption-desorption behavior. A Mo-doped mesoporous material was obtained starting from commercial MSU-H and ammonium molybdate. This mesoporous material (MSU-H-type functionalized with molybdenum salt) was used as support in order to impregnate $LiBH_4$. Even though the thermodynamics of $LiBH_4$ hydrogen absorption-desorption is not modified, the desorption kinetics of supported $LiBH_4$ is improved compared to that of pure $LiBH_4$. Moreover, after re-hydrogenation at 450 ^{0}C only 3.2 wt. % H_2 of storage capacity is recovered for $LiBH_4$, while for supported $LiBH_4$ we achieved almost 5.2 wt. % H_2.

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1. Introduction

The high demand for green energy, the danger of greenhouse effect and the ever more scarce fossil fuels, in the fuel cell (F.C.) vehicles era have made researchers to concentrate on finding some alternatives to classic combustion. Among them, metal borohydrides have been investigated recently as hydrogen storage materials due to their high content of hydrogen by weight (wt% H_2), but the desorption temperature have to be tuned for F.C. usage. $LiBH_4$ (lithium tetrahydroborate) is one of the most studied and promising borohydride; it features a high theoretical total hydrogen storage capacity (18.4 wt. %) and volumetric capacity (121 kg/m^3)[1]. However, the high decomposition temperature of the LiH (over 600 ^{0}C) makes the second dehydrogenation step of $LiBH_4$ less important, limiting the storage capacity to a lower value, 13.8 wt. %, according to reaction (1) - the first decomposition step given below:

$$LiBH_4 \rightarrow LiH + B + 3/2\, H_2 \quad (1)$$

$$LiH \rightarrow Li + 1/2\, H_2 \quad (2)$$

The high decomposition enthalpy (69 kJ/mol H_2) for the first decomposition step proves that the reaction is not reversible under mild pressure-temperature (p-T) conditions, but the complete re-hydrogenation can be achieved under more drastic conditions (600 ^{0}C, and 350 bar H_2) [2].

The kinetic properties of $LiBH_4$ have been improved by ball-milling with metal chlorides [3] and SiO_2 powder [4]. The results show a decrease of the desorption temperature with almost 200 ^{0}C. On the other hand a similar effect may be obtained by maintaining the hydride grains at nanometric scale during the de-hydrogenation – re-hydrogenation reactions. This helps by shortening the diffusion paths of hydrogen during hydride formation/decomposition. As the nanopores decrease in diameter, approaching the 1 nm value, the surface energies become much larger and a possible thermodynamic destabilization of the original hydride may be achieved. Such results have already been presented in literature, for ammonia borane impregnated onto mesoporous silica [5]. Au et al. have prepared $LiBH_4$ with $TiCl_3$ and $MgCl_2$ addition [6]. Their composites desorb 5% H_2 below 450 ^{0}C and reabsorb 4.5 wt % at 600 ^{0}C under 70 bars H_2. Dehydrogenation kinetics of $LiBH_4$ can be improved by impregnation into mesoporous carbon aerogel [7]. Highly active mesoporous materials can be obtained by functionalizing the bulk mesopores with metal sites, obtaining new materials with various applications (such as CO oxidation, catalysis) [8].

Our paper targets the improvement of the kinetics for the hydrogen absorption/desorption reactions for $LiBH_4$. We prepared Mo-functionalized MSU-H and used it as support for $LiBH_4$ impregnation. The present work proves the improvement of desorption kinetics for supported $LiBH_4$ compared to unsupported $LiBH_4$ and the increase of H_2 amount reversibly stored below 450 ^{0}C.

2. Experimental

Starting materials were $LiBH_4$ (95%, Alfa Aesar), MSU-H (purum, Sigma-Aldrich) and $(NH_4)_6Mo_7O_{24}.4H_2O$ (99%, Fluka). The mesoporous MSU-H was impregnated several times with hot, saturated molybdenum salt (MSU-H / Mo salt weight ratio 10.3 / 1); the reaction comprised in two steps: heating both degassed MSU-H and the ammonium molybdate at 90 ^{0}C, and afterwards further heating to 150 ^{0}C. The impregnation effectiveness was increased by repeating these two steps, until total solution consumption. The resulted composite MSU-H: molybdate was introduced in an oven and calcined in air at 550 ^{0}C, for 4 hours. At this temperature, the molybdate anions decompose and MoO_3 phase results. The subsequent treatment in hydrogen flow of the modified MSU-H involves Mo^{6+} reduction to Mo, therefore the obtained material will be denoted as Mo:MSU-H. The advantage of using hot impregnation is that the MSU-H will be filled by the precursor solution, and the decomposition step creates metal free sites inside the MSU-H pores.

Afterwards, $LiBH_4$ was melt impregnated into Mo doped MSU-H , at the $LiBH_4$ melting point (270 ^{0}C) starting from the mixture of materials (weight ratio 5:1). The resulted composite will be denoted $LiBH_4$-Mo:MSU-H in the followings. The samples manipulation was done into a MBraun glove box under purified Argon (<1 ppm O_2, <1 ppm H_2O) in all the stages of the work. X-Ray diffraction measurements were performed using a D-8 Advance Bruker diffractometer with Cu-Kα radiation. The samples were covered with a thin polymeric layer in order to avoid oxidation during XRD measurements. Thermal programmed desorption measurements (TPD) and kinetic measurements were obtained using a commercially available volumetric Sievert apparatus provided by Advanced Material Corporation, Pittsburg USA. Hydrogen evacuation from samples was done using a dual stage rotary pump (ultimate pressure 10^{-3} Torr). The pressure sensors had a resolution of 0.2 bar.

3. Results and discussion

Fig. 1 shows the XRD data for commercial MSU-H and Mo-doped MSU-H (Mo:MSU-H) synthesized as described in the experimental section of the paper. The XRD patterns of the samples are almost identical. The very broad peak at about 22.3 degrees is a fingerprint of these structures. There is no evidence of Mo in the XRD pattern of Mo:MSU-H due to the very high dispersion inside the MSU-H matrix.

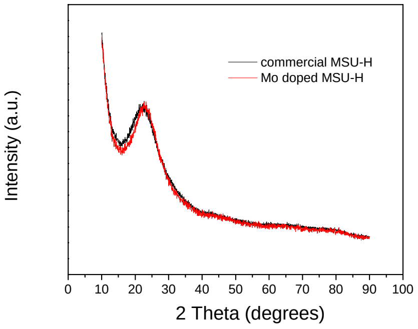

Fig. 1. XRD data of MSU-H samples (commercial and Mo doped).

Fig. 2 shows the XRD pattern of the commercially $LiBH_4$ (A) (named as SI), $LiBH_4$ – Mo:MSU-H composite (named as SII) in re-hydrogenated state (B) and SII in de-hydrogenated state (C). The original $LiBH_4$ has a monoclinic crystalline structure, but after impregnation onto Mo:MSU-H the peaks of this phase cannot be observed for the re-hydrogenated sample, contrary to what is expected after hydrogen uptake (Fig. 2 B). The reason is that $LiBH_4$ has a very disordered structure after melt impregnation onto the mesoporous Mo:MSU-H, and this is sustained by the presence of a very broad peak at about 2 Theta = 28^0. This amorphous contribution is more obvious in the XRD graph of the re-hydrogenated sample (Fig. 2 B) rather than that of the de-hydrogenated sample (Fig. 2 C), as one would expect from the decomposition reaction (1). The crystalline phase which appears clearly for both XRD patterns (Fig. 2 B and Fig. 2 C) is Li_4SiO_4. This phase is formed at the $LiBH_4$ – Mo:MSU-H boundary and it substantially improves the hydrogen desorption kinetics and enhances the amount of hydrogen that can be reversibly stored below 450 ^{0}C compared to $LiBH_4$. This statement is sustained by the following kinetics measurements.

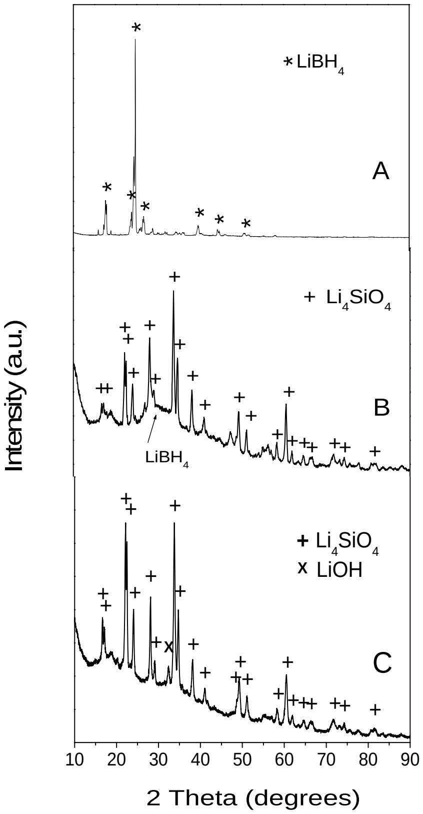

Fig. 2. XRD data of commercial $LiBH_4$ (A) ,re-hydrogenated $LiBH_4$ - Mo:MSU-H (B) and de-hydrogenated $LiBH_4$ Mo:MSU-H (C).

Fig. 3 exhibits the thermal programmed desorption data for $LiBH_4$ (SI) and $LiBH_4$ mixed with Mo:MSU-H (SII) for as prepared samples (the first desorption curve). The mass ratio for the second sample was 5:1 ($LiBH_4$: Mo-MSU-H) as estimated for a 70% filling of the pores inside MSU-H matrix by $LiBH_4$. The impregnation occurs at about 270 ^{0}C, the melting point of $LiBH_4$.

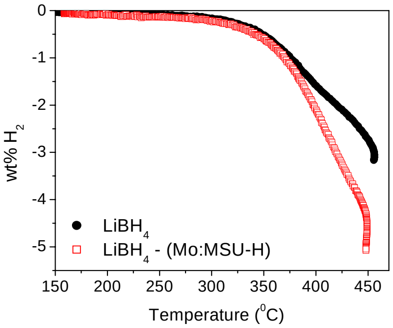

Fig. 3. Thermal programmed desorption data of commercial $LiBH_4$ and impregnated $LiBH_4$ –Mo:MSU-H.

The temperature was increased with 5 ^{0}C / min from 150 ^{0}C up to 450 ^{0}C. The amount of hydrogen desorbed below 450 ^{0}C for both samples, is almost identical, 11.2 wt% H_2 and the desorption starts at about the same temperature, but the most important part of desorption occurs at lower temperatures for the $LiBH_4$ – Mo:MSU-H.

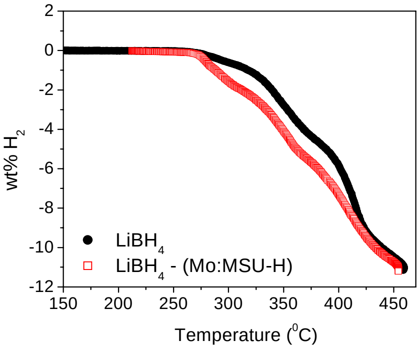

Fig. 4. Thermal programmed desorption data of re-hydrogenated samples: $LiBH_4$ and impregnated $LiBH_4$ – Mo:MSU-H.

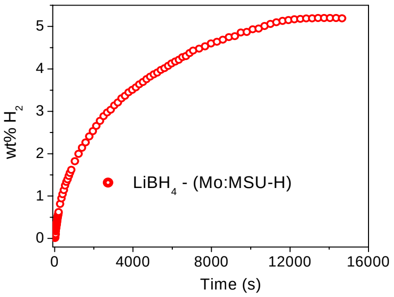

Fig. 5. Re-hydrogenation kinetics for $LiBH_4$ – (Mo:MSU-H).

Fig. 4 presents the thermal programmed desorption curves for the same samples after the re-hydrogenation. The amount of hydrogen desorbed is less than that obtained for the first desorption. For re-hydrogenated SII the presence of Li_4SiO_4 phase decreases the amount of the hydrogen storage capacity down to a theoretical 6.5 wt% assuming a total consumption of the silica matrix by the reaction with $LiBH_4$. This is not the case of SI where only an incomplete re-hydrogenation reaction below 450 ^{0}C may explain the drastic loss of the storage capacity. After re-hydrogenation the sample SI releases only 3.2 wt% H_2 while SII desorbs about 5.2 wt% H_2 at temperatures below 450 ^{0}C. The reversible stored amount of hydrogen for SII approaches well the theoretical value of 6.5 wt% but for SI is far below the theoretical value of about 13 wt% H_2 In any case the impregnation into silica matrix helps concerning the maximum wt% H_2 which can be recovered after the de-hydrogenation and also it improves the desorption kinetics compared to as received $LiBH_4$.

Fig. 5 shows the re-hydrogenation kinetics curve at 450 ^{0}C, under 80 atm H_2 for SII. The maximum hydrogen content by weight which can be absorbed is 5.2 wt% . This value is comparable with that previously obtained [6] for $LiBH_4$ – $TiCl_3$ – $MgCl_2$ composites, but achieved only at higher temperature, 600 ^{0}C. These results proves once again the effectiveness of impregnation method (in our particular case – $LiBH_4$ – Mo:MSU-H) to improve both the absorbtion and the desorption kinetics compared to unsupported $LiBH_4$.

4. Conclusions

$LiBH_4$ was melt impregnated into Mo:MSU-H mesoporous sieve. The results clearly show substantial improvement compared to $LiBH_4$ concerning the maximum re-hydrogenation yield (5.2 wt% H_2 for impregnated $LiBH_4$ compared to 3.2 wt% H_2 for as-received $LiBH_4$ both obtained at 450 ^{0}C under 80 atm H_2). Also the desorption kinetics is faster for $LiBH_4$ – Mo:MSU-H compared to $LiBH_4$. Results for other hydrides impregnated into such mesoporous materials will be published in a forthcoming paper.

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