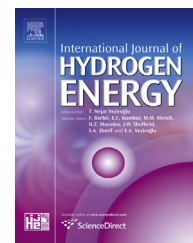




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Carbon supported lithium hydride nanoparticles: Impact of preparation conditions on particle size and hydrogen sorption

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ABSTRACT

Nanosizing of light metal hydrides has yielded significant improvements to their hydrogen storage properties. We explored for the first time a procedure for preparing supported LiH nanoparticles. Impregnation of a carbon framework with a butyllithium solution, followed by reaction with gaseous hydrogen yielded LiH particles ranging in size from 2 nm to the micrometer scale. Reducing the reaction temperature from 300 °C to 100 °C, as well as the use of a t-butyllithium precursor instead of an n-butyllithium precursor, gave significant improvements on the degree of confinement of the LiH particles. The particle size of the LiH has a significant impact on the hydrogen release profile, 11 nm crystallites begin to release hydrogen as low as 100 °C under argon flow, a reduction of roughly 400 °C on the macrocrystalline system. The hydrogen release is reversible, with hydrogen uptake after desorption as high as 7.0 wt% w.r.t. LiH (0.8 wt% w.r.t the sample) under 0.1 bar of hydrogen at 200 °C and full uptake takes place within 5 min at 26 bar. This new preparation procedure for supported light metal hydrides is particularly relevant for the field of hydrogen storage.

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Introduction

Light metal hydrides have been investigated for a range of applications including hydrogen storage [1–3] (due to their high gravimetric hydrogen densities) and batteries (in electrodes and solid state electrolytes) [4]. Ideal properties for metal hydrides for the solid state storage of hydrogen for vehicular application are high gravimetric and volumetric hydrogen densities, low temperatures of hydrogen release and uptake, fast kinetics and reversibility. No material has so far been found to possess each of these characteristics but

light metal hydrides have displayed the most promise, where modification of the material is hoped to improve their hydrogen sorption characteristics such that they could be viable for application [5–7].

MgH₂ [8–10] and NaH [11] are prominent examples of light metal hydrides investigated for hydrogen storage as they can store 7.6 wt% and 4.2 wt% of hydrogen respectively. A similar, somewhat overlooked, hydride with great promise is lithium hydride, LiH, which contains 12.6 wt% of hydrogen [9,12]. The main reason LiH has not been as extensively studied as other hydrides is that it only releases hydrogen at temperatures above 500 °C, but this might be improved through a number of

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methods. For instance, in general reducing the particle and crystallite size of metal hydrides improves the kinetics of sorption due to shorter diffusion distances of hydrogen while also demonstrating lower temperature of release and enhanced reversibility [13,14]. Additionally, interaction between carbon and Li-based hydrides gives a reduction in hydrogen release temperature due to the reversible intercalation of Li between the graphene sheets promoting decomposition of the hydride [15,16].

Many techniques have been studied in the preparation of small crystallites and particles of light metal hydrides such as ball-milling [17,18] and confinement into a porous matrix [19]. For example, vapor deposition of MgH_2 into a carbon xerogel support has been used to produce MgH_2 particles in the 6–20 nm range [20]. The particle size was controlled by tuning the pore size of the carbon support and the smaller particles demonstrated hydrogen release at temperatures 140 °C lower than the macrocrystalline system under argon flow. Melt infiltration has also been a very useful technique in preparation of a number of metal hydride nanocomposites such as NaAlH_4/C [21], which demonstrates a 150 °C reduction in hydrogen release temperature compared to the macrocrystalline system.

However, there are few known examples of the preparation of supported LiH nanoparticles [22–24]. This can be attributed to the fact that many of the common preparation techniques cannot be readily applied to LiH. The high temperatures required to melt LiH initiate reaction between LiH and the carbon support, which means melt infiltration and vapor deposition cannot be used in this case [25,26]. There are a number of alternative methods that have been proposed such as electrochemically inserting lithium into graphite and subsequent hydrogenation to produce nanostructured LiH. This nanostructuring reduces the onset temperature of hydrogen release to 200 °C under argon flow and a total hydrogen capacity of 0.96 wt% [27].

Solution based techniques, such as solution impregnation, are widely used methods of producing nanocomposites [28]. A number of parameters can influence particle size such as the conditions under which the particles are formed. For example, in preparation of supported metal particles from aqueous metal salt precursors the drying step is essential as removal of solvent before precipitation of the metal yields migration of the metal particles to the external surface of the support [28]. For this reason low temperature drying is often necessary. In addition, nucleation sites within the pores facilitate the growth of particles in the pore system and so the density of nucleation sites can be critical to the efficiency of confinement of the particles [28]. Thus, the drying step in solution impregnation techniques is crucial to particle size control and a number of experimental parameters can be tuned to this effect.

However, LiH is insoluble in most solvents [29], and it is therefore necessary to use a precursor from which the desired LiH can be formed. In solution impregnation the loading is limited by the solubility of the precursor as more concentrated solutions allow a higher loading. Incipient wetness impregnation, where the amount of solution equivalent to the pore volume of the support is used, ensures that all of the active component is contained to the pores but this produces low

loadings. MgH_2 nanoparticles have been successfully prepared on a carbon support by impregnation with a dibutylmagnesium precursor followed by decomposition and reaction with hydrogen at 300 °C [30,31]. The resulting MgH_2/C nanocomposite gave faster hydrogen release kinetics than ball-milled samples and demonstrated 75% reversibility [30].

Herein we present a procedure, which builds on the previously reported method for supporting MgH_2 nanoparticles [30], for the preparation of a new nanocomposite: LiH/C. This is done by solution impregnation and subsequent reaction of a butyllithium precursor followed by drying under vacuum at room temperature. A number of experimental parameters were varied with the goal of reducing the average particle size of the LiH particles. This includes the type of carbon support, the type of butyllithium precursor and the temperature at which the reaction is performed. This newfound understanding of the solution impregnation procedure can be applied to the preparation of other similar compounds.

Experimental

Materials: *n*-butyllithium (*n*-BuLi, 2.5 M in hexanes) and *tert*-butyllithium (*t*-BuLi, 1.7 M in pentane) were obtained from Sigma–Aldrich. Hydrogen gas was obtained from Linde with a purity of 99.999999%. Butyllithium (BuLi) solutions were stored in a nitrogen-filled glovebox (Mbraun Labmaster I30, 1 ppm H_2O , <1 ppm O_2) prior to use.

Carbon supports: Two different supports were used: carbon xerogel (CX18) and high surface area graphite (HSAG). The carbon xerogel support was prepared using the sol–gel resorcinol procedure [32] and is an amorphous carbon support consisting of micron to millimeter-sized particles containing intra-particle pores. CX18 has a volume average pore diameter of 18 nm. HSAG was obtained from TimCal and is a graphitic-type support with a pore size that ranges from 2 to 50 nm in diameter. It comes in a powder form and consists mostly of graphite sheets. All carbon types were dried under argon flow at 600 °C for 12 h and characterized using X-ray diffraction and nitrogen physisorption before use.

Preparation of the nanocomposites: The LiH/C nanocomposites were prepared by filling a Parr 30 cm^3 autoclave with 10 cm^3 of the butyllithium solution in a nitrogen-filled glovebox, and then adding 1 g of carbon support on top, allowing it to sink to the bottom to ensure complete wetting. The autoclave was then sealed, removed from the glovebox, pressurized with 50 bar hydrogen and heated while stirring for 20 h. Afterwards the autoclave was allowed to cool to room temperature before venting the gas and applying vacuum with a cold trap for 2 h to remove the solvent. The final powder product was then stored in an argon-filled glovebox (Mbraun Labmaster dp, 1 ppm H_2O , <1 ppm O_2) before analysis. With the aim of studying the effect of parameters such as support type, precursor type and temperature of decomposition a number of different nanocomposites were prepared, the details of which are recorded in Table 1. The naming convention used in Table 1 is divided into several parts, each divided by an underscore. The first part refers to the support used, the second refers to the butyllithium isomer used (*t* = 1.7 M *tert*-butyllithium in pentane, *n* = 2.5 M *n*-butyllithium in hexanes) and the third indicates

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