

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

Hydrolysis of lithium hydride under low relative humidity

J. Guichard ^{a,b}, F. Bouyer ^b, E. Sciora ^b, F. Bernard ^b, H. Lecoq ^a,
R. Besnard ^a, J.P. Bellat ^{b,*}

^a CEA, DAM, Valduc, 21120 Is sur Tille, France

^b Laboratoire Interdisciplinaire Carnot de Bourgogne UMR 6303 CNRS, Université Bourgogne Franche-Comté, 9 Avenue Alain Savary, BP 47870, 21078 Dijon Cedex, France

ARTICLE INFO

Article history:

Received 20 May 2015

Received in revised form

7 July 2015

Accepted 10 July 2015

Available online 15 August 2015

Keywords:

Lithium hydride

Hydrolysis

Adsorption

ABSTRACT

Hydrolysis of LiH at room temperature and under low relative humidity (RH < 2%) is studied by manometry working with heavy water either in closed (variable water vapor pressure) or open (constant water vapor pressure) system. Products of the reaction are characterized by XRD and FTIR. It is shown for the first time that the hydrolysis reaction occurs in two steps: first water is adsorbed on the LiH surface and then the hydrolysis reaction starts. In open system, for relative humidity lower than 0.04% only the formation of Li₂O is observed while for higher moisture the reaction continues with the production of LiOD. The reaction rate is however extremely low and only a very small amount of LiH is transformed. The kinetic can be well predicted by the model of core shrinking limited by the diffusion through the layer of Li₂O and/or LiOD surrounded LiH particles. For practical application, it is concluded that if LiH is stored under controlled humidity lower than 0.04% (40 ppm) there is no major risk to form LiOH in significant amount.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Lithium hydride, LiH, and its derivatives are very attractive materials, particularly in the field of new energy technologies such as controlled fusion, hydrogen fuel cells and neutron shielding [1–3]. Lithium hydride has been extensively studied as hydrogen storage materials. Its absorption capacity of about 2000 cm³_{STP}.cm⁻³, its low density (0.8 g cm⁻³) and its decomposition process that does not require thermal activation, make this material a suitable hydrogen storage medium [4–6]. LiH is also a potential candidate for the hydrogen production. Due to its very high reactivity with water yielding

hydrogen it could be used as hydrogen generator [7,8]. However to be attractive in the development of low power energy devices as fuel cells, the kinetic of the reaction of hydrogen desorption and hydrolysis of LiH are still too slow and must be considerably improved. Moreover, some applications as lithium batteries and nuclear power engineering require to protect lithium derivatives (LiH, Li₂O) from water. It is well known that the ageing and the durability of these materials are strongly dependent on the degree of humidity of their environment. Actually, lithium hydride is a material whose implementation requires a stringent control of the air handling and/or air storage. Indeed, this material is extremely

* Corresponding author.

E-mail address: jean-pierre.bellat@u-bourgogne.fr (J.P. Bellat).

<http://dx.doi.org/10.1016/j.ijhydene.2015.07.047>

0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

hygroscopic: the reaction of lithium hydride with water is highly exothermic and generates the release of molecular hydrogen. As a consequence, it must be handled in a glove box, under dry atmosphere and inert gas, to prevent any risk of inflammation [9]. This is the reason why it is of a relevant interest to study the kinetic of the reaction of LiH with H₂O in order to be able to predict the behavior of this material in the presence of water.

Numerous research groups have investigated the LiH hydrolysis by using various experimental techniques, as described in the review of Heartling [10]. They agree that during hydrolysis a dual LiH/Li₂O/LiOH interface is formed and that Li₂O plays the role of a protective layer affecting the diffusion of water towards LiH [11]. However, due to the high reactivity of this material with air and the various experimental conditions, many hypotheses are suggested to describe the overall reaction scheme of the LiH hydrolysis. Most of these studies exhibit contradictory conclusions regarding the reaction schemes and the species involved. A few decades ago, Machin and Tompkins were the first to study the reaction kinetics between water vapor and crystals of LiH [12]. They exposed LiH crystals to several equivalent doses of water vapor (i.e. in a closed system) at room temperature. They showed that if the amount of water introduced in the system can react with one or less than one LiH monolayer, Li₂O is formed. But if the amount of water is sufficient to react with several LiH layers, the reaction leads to the formation of LiOH. Maupoix et al. [13] studied the hydrolysis of LiH in open system by exposing the sample to an argon flow with a water vapor partial pressure of 25 hPa. They only observed the formation of anhydrous lithium hydroxide LiOH or the monohydrate form LiOH·H₂O. Li₂O was not detected. However, Shuia [14] and Xiao [15] showed, with experiments performed in open system under a water vapor pressure of 0.2 hPa, that the hydrolysis of LiH starts with the formation of Li₂O and continues with the formation of LiOH.

Several other researches were devoted to the reaction kinetics of LiH. Wilson et al. [16], Broughton et al. [17] and Maupoix et al. [13] clearly demonstrated that the reaction kinetics is strongly influenced by the temperature, the water vapor pressure, the amount of material, the grain size or the powder compaction level.

To summarize, the reaction of LiH with water is not still clearly elucidated. Some questions remain open. For example, does hydrolysis of LiOH lead to the formation of Li₂O and/or LiOH according to the moisture level? Therefore for using LiH in industrial applications in the best conditions, it is of great importance to have a more detailed knowledge about the reactivity of LiH with water.

The aim of this work is then to revisit the hydrolysis reaction of LiH especially under low relative humidity in order to clearly and definitively identify which phases (Li₂O and/or LiOH) are produced during the reaction and to establish a kinetic model. For that, the hydrolysis of LiH is studied by using the manometry technique in conditions similar to those found in industrial applications. Experiments are performed either in closed system (variable water vapor pressure) with H₂O as limiting reagent or in open system (constant water vapor pressure) with LiH as limiting reagent. From these two methods it is possible to determine the extent of the reaction

with time by measuring the change of pressure during the reaction. Thus, it is possible to identify which reaction proceeds (formation of Li₂O or LiOH) and which kinetic model is the most appropriate to describe the extent of reaction with time. In addition, the obtained phases after reaction are characterized by using infrared spectroscopy (FTIR) and X-ray diffraction (XRD).

Experimental

Materials

All samples of LiH are extracted from a same batch of powder purchased from the chemical company Acros Organics with a purity of 97%. All handling and preparation are performed in dry argon ($P_{\text{H}_2\text{O}} < 0.04$ hPa) filled glove box in order to avoid atmospheric contamination (H₂O, O₂, CO₂...).

Equipment

A specific manometric setup has been constructed in-house by using the high vacuum technology to achieve hydrolysis experiments in a large range of light (H₂O) or heavy (D₂O) water vapor pressure (10^{-4} –30 hPa) at room temperature (Fig. 1). This device allows performing hydrolysis either under variable (closed system) or constant (open system) water vapor pressure. For experiments in closed system, a single dose of heavy water vapor (D₂O) is introduced in the intermediate compartment leading to a pressure P_E while the sample (0.5 g of LiH) is in the reaction compartment under vacuum. At the initial time, t_0 , the valve, V_2 , is opened and the pressure goes down to an initial pressure P_0 due to the release of the gas in the volume V_R before the reaction starts. Then the hydrolysis reaction is studied by measuring the total pressure in the system every 1 s for 1 h and every 10 s for the rest of the experiment. The initial pressures P_0 of water in this device at room temperature are ranging from 0.4 to 9 hPa (Table 1).

For experiments in open system, the reserve of liquid water in equilibrium with its gas phase is maintained at constant temperature by using a cryostat. At the initial time, t_0 , the valves V_1 and V_2 are opened in order to put the sample under constant saturated water vapor pressure. Then, the total pressure is recorded as a function of time (every 1 s for 1 h and every 15 s for the rest of the experiment). The partial pressure of hydrogen or deuterium produced by the reaction is obtained by subtracting the constant saturated water vapor pressure to the total pressure. Then, the extent of the reaction can be calculated from this partial pressure assuming the gas as ideal. The values of the constant vapor pressure of D₂O lie between 0.01 and 0.17 hPa (Table 2). The volumes of the setup have been previously calibrated by helium pycnometry. Before each hydrolysis, a blank experiment is performed without sample and in the same conditions to take into account the change of the pressure due to unavoidable leaks and adsorption phenomena of water on the walls of the manometric device.

XRD experiments are performed with a goniometer D8 ADVANCE from Bruker equipped with a linear counter VANTEC-1 using $K\alpha_1$ copper radiation ($\lambda = 1.540598$ Å). To

Download English Version:

<https://daneshyari.com/en/article/1278792>

Download Persian Version:

<https://daneshyari.com/article/1278792>

[Daneshyari.com](https://daneshyari.com)