

Effects of Li_2O Thickness and Moisture Content on LiH Hydrolysis Kinetics in Slightly Humidified Argon

S. Xiao, M. B. Shuai and M. F. Chu

Abstract—The hydrolysis kinetics of polycrystalline lithium hydride (LiH) in argon at various low humidities was measured by gravimetry and Raman spectroscopy with ambient water concentration ranging from 200 to 1200 ppm. The results showed that LiH hydrolysis curve revealed a parabolic shape, which was attributed to two different reaction stages that forming different products as explained by the ‘Layer Diffusion Control’ model. Based on the model, a novel two-stage rate equation for LiH hydrolysis reactions was developed and used to fit the experimental data for determination of Li_2O steady thickness H_s and the ultimate hydrolysis rate vs. The fitted data presented a rise of H_s as ambient water concentration c_w increased. However, in spite of the negative effect imposed by H_s increasing, the upward trend of v_s remained, which implied that water concentration, rather than Li_2O thickness, played a predominant role in LiH hydrolysis kinetics. In addition, the proportional relationship between $v_s H_s$ and c_w predicted by rate equation and confirmed by gravimetric data validated the model in such conditions.

Keywords—Hydrolysis kinetics, ‘Layer Diffusion Control’ model, Lithium hydride

I. INTRODUCTION

LITHIUM HYDRIDE (LiH), combining of high hydrogen density and low mass density, is an attractive material as neutron shield, reactor fuel and hydrogen sources [1],[2]. However, its high affinity of water, resulting in considerable hydrogen and heat releasing, has brought up a number of challenges on safety and validity issues during handling and storing this material.

Recent studies on the products and kinetics of reactions between LiH and water, generally named ‘hydrolysis’, were completed for a wide range of conditions [3]. In spite of the multitude of material types, water concentrations and environmental gases, as well as the diversity of experimental techniques, the LiH hydrolysis studies had commonly arrived at some agreements as following: (i) The ‘tri-layer’ model [4],[5] of LiH hydrolysis products. As described in the model, LiOH is the predominant solid product for reactions at room temperature, ambient pressure and water concentrations below 523 Pa; Li_2O is another product that has been both theoretically [4],[6] and experimentally [7] proved to exist as a layer at the

interface of LiH and LiOH. (ii) The ‘parabolic’ reaction kinetics [8]-[10]. A number of results on LiH hydrolysis showed a parabolic rate behavior, that is, a parabola-like stage followed by a linear one. Although these ideas were supported by abundant evidence, several issues, such as the intrinsic factors that attributed to the ‘odd’ parabolic rate behavior, remained unclarified.

For a detailed understanding of the reasons why LiH hydrolysis showed such a parabolic rate behavior, the relationship between the hydrolysis rate and the composition of products should be uncovered first. Some researchers [9],[11],[12] proposed their own models of LiH hydrolysis kinetics, attempting to clarify this relationship. One of the researchers, Haertling [1], with his co-workers, developed a novel model named “Layer Diffusion Control”, which described the formation and growth of hydrolysis products on the basis of Rutherford backscattering analysis for LiH exposed to water vapor. Within the model, the Li_2O thickness, which varied with temperature, pressure and water concentration, was postulated to be the key factor that controlled the overall hydrolysis rate of LiH. The model explained the ‘parabolic’ behavior in LiH hydrolysis rate, as well as the effects of temperature, pressure and water concentration, and coordinated with the present body of literature. Nevertheless, the existing database is insufficient to unequivocally buttress all key aspects of the model. Additional experiments are required to evaluate the Li_2O thickness and establish its relationship with the hydrolysis rate. Moreover, the initial parabola-like reaction stage needs a detailed study for full understanding of LiH hydrolysis.

The present work was designed to provide extra experimental data for Haertling’s model and also to validate it. Quantitative data for a range of humidities were collected with the intent of evaluating the Li_2O thicknesses and hydrolysis rates with various water concentrations. The data were also a supplement to the present database for LiH hydrolysis rate as a function of water concentration.

II. EXPERIMENTAL

A. Sample Preparation

The LiH samples here were cylindrical compacts of LiH particles with a density of 0.76 g cm^{-3} . The compacts were then machined to a size of $\sim 2 \text{ cm}$ in diameter and 1 cm in thickness. Prior to exposure, they were ground with SiC paper to a $19\text{-}\mu\text{m}$ finish in a glovebox filled by argon. Fig. (1) is the optical and

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SEM images of a typical sample. The sample was even and homogenous except for a few cracks. Finally, the geometric parameters of the samples were measured by a vernier caliper.

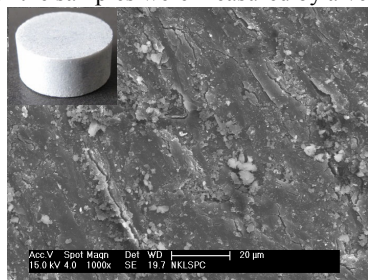


Fig. 1 Optical and SEM images for a typical LiH sample

B. Sample Exposure

Sample exposure was carried out at 298 K, in the same glovebox where the samples were ground. The water concentration and the total pressure in the glovebox were monitored instantly and adjusted by a controlling system. Before each experiment, the water concentration was preset to a certain value. During the entire exposure, the total pressure was maintained at a few hundred Pa higher than atmospheric pressure to decrease the possibility of ambient gaseous contaminants penetrating into the glovebox.

C. Analysis

Gravimetry was implemented by placing the exposing samples onto an electronic balance with a precision of 0.01 mg and monitoring the weight variation during the exposure. The weight was recorded every 5 min for the first hour, and the interval extended to 10–20 min afterwards. Raman spectra were collected by an Almega XR Dispersive Raman spectroscope (Thermo Fisher Scientific Co., USA). The laser power on the samples was 20 mW at the wavelength of 532 nm. Each Raman spectrum was due to the result of 20 scans and the resolution of the spectrometer was 2 cm^{-1} .

III. RESULTS AND DISCUSSION

A. Gravimetry

Considering the difference in surface area of the samples and assuming that LiH hydrolysis rate is proportional to its surface area, we normalized the hydrolysis rate to weight gain per minute on a unit area. Fig. 2 showed the LiH weight gain vs. exposure time for exposure to H_2O concentrations of 200, 400, 700 and 1200 ppm. The curves in Fig. 2 presented two different stages: an initial rise followed by a linear slope. The weight gain started with a high rate but slowed down gradually in the first stage and grew at a constant rate in the second one. The gravimetric data were consistent with some other experiments [8]–[10],[13] on LiH hydrolysis, all of which presented such a ‘paralinear’ behavior of hydrolysis rates in spite of the diversity of experimental methods.

It was noticed that all the curves revealed a paralinear shape but with different initial and ultimate rates. The ultimate rates were typically $1 \times 10^{-7}\text{ g cm}^{-2}\text{ min}^{-1}$ to $1 \times 10^{-6}\text{ g cm}^{-2}\text{ min}^{-1}$ and

increased with water concentration. These data demonstrated that LiH hydrolysis rate was a function of water concentration and increased with the concentration. Two curves intercrossed in the initial period, probably attributed to the difference in delayed zero time relative to the ‘true’ starting time of hydrolysis. The difference between the two time points would be discussed in the next sections.

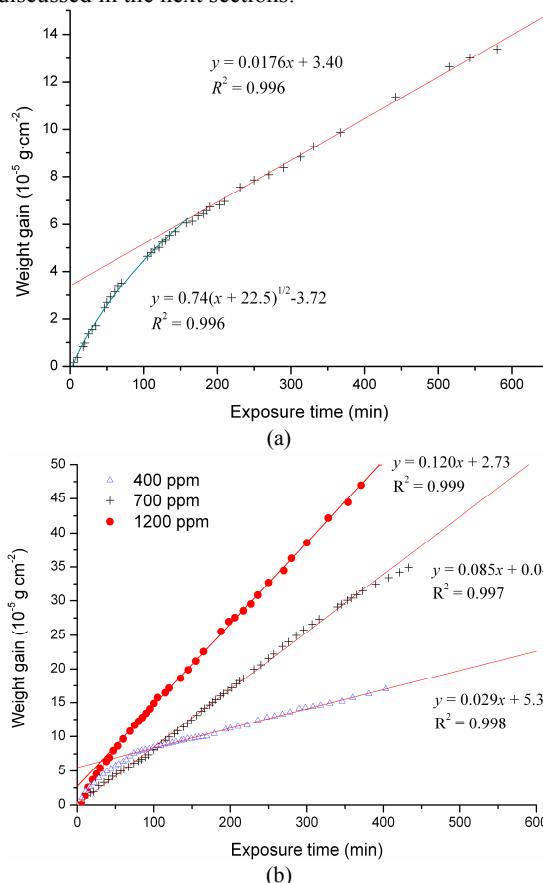


Fig. 2 Weight gain curves of LiH exposed to 200 ppm (a), 400 ppm, 700 ppm and 1200 ppm H_2O (b). The linear section of each curve is fitted by Eq. 11.

B. Raman Spectra

Raman spectra of LiH exposed to 200 ppm H_2O for different time were shown in Fig. 3. The exposure time was 0, 0.5, 1, 2, 3 and 6 h. To distinguish them from each other, all the spectra were shifted vertically and arranged by exposure time. It was shown that a relatively narrow band appeared at 3665 cm^{-1} accompanied by a broader band centered at $\sim 490\text{ cm}^{-1}$. The broad band centered at about 490 cm^{-1} could originate from a Li_2O disordered phase, which appeared immediately the sample was prepared and always existed for the later 6 h. Likewise, the band at 3665 cm^{-1} was assigned to OH stretching of the hydroxyl in LiOH, which was notably observed only after a delay of about 3 h. There was a coincidence that the critical time when gravimetric curve went linear was comparable to the time when the Raman band of LiOH turned up. This coincidence implied a potential relationship between the hydrolysis rate and the reactions forming different products.

Additionally, the inevitable Li_2O formation prior to exposure at such a low humidity, which was consistent with the phase diagram of Li-O-H system[9], approved the discrepancy between zero time and the 'true' starting time of reaction as mentioned in Section 3.1. The rapid formation of Li_2O had also been observed in other research [14].

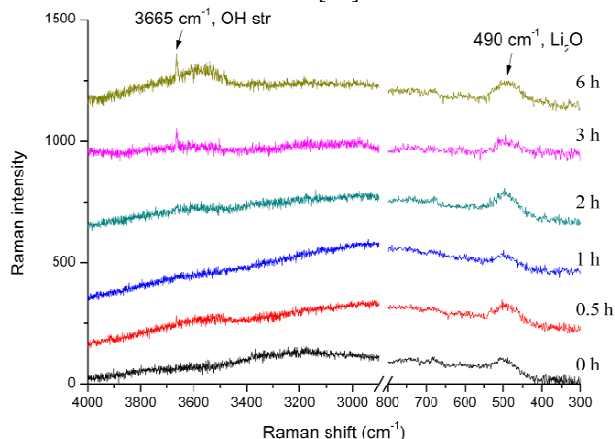


Fig. 3 Raman spectra of LiH samples after exposure to 200 ppm H_2O for 0-6 h. The spectral range of 2900-1100 cm^{-1} is truncated for no Raman bands are observed in the range

The relationship between the 'paralinear' hydrolysis rates and the corresponding reactions had been interpreted by 'Layer Diffusion Control' model, of which the core idea was that diffusion in Li_2O layer determined the overall hydrolysis rate and the thickness of Li_2O layer acted as the key factor. According to that model, Li_2O was the product formed in the parabola-like stage and went thicker with time, resulting in a thickening Li_2O layer and a consequent decreasing hydrolysis rate; whereas in the linear stage two reactions simultaneously occurred at both sides of Li_2O layer and Li_2O was both produced and consumed at the same rate, resulting in a steady Li_2O thickness and a consequent stable hydrolysis rate. The Raman spectra coordinated well with the model.

Nonetheless, quantified data on the relationship between Li_2O thickness and the hydrolysis rate were still absent, probably due to the difficulty in determining the Li_2O thickness. For Li_2O layer was considered to be extremely thin[15] and quite reactive with ambient gases in common conditions, few techniques were feasible to directly observe its thickness even in a moderate precision. Here we reified and quantified the 'Layer Diffusion Control' model and introduced a novel rate equation for LiH hydrolysis, for the purpose of evaluating the Li_2O thickness by gravimetric data.

C. Hydrolysis Rate Equations

Based on Haertling's model, a novel equation for LiH hydrolysis rates was developed. Considering the difference in reaction mechanisms, we deduced the rate equation individually for the two stages separated by the critical time t_c :

i) In the first stage ($0 \leq t \leq t_c$), Li_2O is the product and the rate-determining step is diffusion through the Li_2O layer. Fick's first law for diffusion can be written as:

$$J = -D \frac{c_1 - c_0}{H(t)} \quad (1)$$

where J is the flux ($\text{mol cm}^{-2} \text{min}^{-1}$), D is the diffusion coefficient ($\text{cm}^2 \text{min}^{-1}$), $H(t)$ is the Li_2O thickness (cm) at time t , and c_1 and c_0 are the diffusant concentrations at the inner and outer face of the layer (mol cm^{-3}), respectively. Assuming that the reaction at the inner face is much faster than the diffusion through the layer itself, $c_1 \approx 0$. On the other hand, for the duration from t to $t + \Delta t$, n moles of diffusant arrive at the $\text{Li}_2\text{O}/\text{LiH}$ interface on a unit area and react with LiH to thicken the Li_2O layer, where $n = J\Delta t$. Accordingly, the change in Li_2O thickness can be expressed by:

$$H(t + \Delta t) - H(t) = nV_{m,\text{Li}_2\text{O}} = JV_{m,\text{Li}_2\text{O}}\Delta t \quad (2)$$

where $V_{m,\text{Li}_2\text{O}}$ is the mole volume of Li_2O . Substituting (1) into (2) and letting $\Delta t \rightarrow 0$ yields:

$$\frac{dH(t)}{dt} = DV_{m,\text{Li}_2\text{O}} \frac{c_0}{H(t)} \quad (3)$$

with the starting condition of $H(0) = H_0$ (H_0 is the Li_2O thickness at time $t = 0$). The solution of Eq. (3) is:

$$H(t) = (2DV_{m,\text{Li}_2\text{O}}c_0t + H_0^2)^{1/2} \quad (4)$$

Therefore, the rate equation for the first stage can be written as follows:

$$\begin{aligned} m_g(t) &= \rho_{\text{Li}_2\text{O}} (H(t) - H(0)) \\ &= \rho_{\text{Li}_2\text{O}} [(2DV_{m,\text{Li}_2\text{O}}c_0t + H_0^2)^{1/2} - H_0] \\ &= A(t + B)^{1/2} + C \quad (0 \leq t \leq t_c) \end{aligned} \quad (5)$$

where $m_g(t)$ is the weight gain at time t , $\rho_{\text{Li}_2\text{O}}$ is the mass density of Li_2O , $A = \rho_{\text{Li}_2\text{O}}(2DV_{m,\text{Li}_2\text{O}}c_0)^{1/2}$, $C = -H_0\rho_{\text{Li}_2\text{O}}$ and $B = H_0^2 / 2DV_{m,\text{Li}_2\text{O}}c_0 = (C/A)^2$.

ii) In the second stage ($t > t_c$), two reactions occur at either side of the Li_2O layer. One is $\text{LiH} + \text{H}_2\text{O} \rightarrow \text{Li}_2\text{O} + \text{H}_2$, which produces Li_2O , and the other is $\text{Li}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{LiOH}$, which consumes Li_2O . Both reactions quickly approach a balance that Li_2O is both produced and consumed at the same rate, resulting in a Li_2O layer with a steady thickness. Thus, the overall reaction turns into a steady state and the hydrolysis rate becomes constant. The rate-determining step here is also the diffusion through the Li_2O layer and the equation is represented as:

$$J' = -D \frac{c'_1 - c'_0}{H_s} \quad (6)$$

where J' is the flux ($\text{mol cm}^{-2} \text{min}^{-1}$), D is the diffusion coefficient ($\text{cm}^2 \text{min}^{-1}$), H_s is the steady thickness of Li_2O (cm), which can be calculated by:

$$H_s = H(t_c) = (2DV_{m,\text{Li}_2\text{O}}c_0t_c + H_0^2)^{1/2} \quad (7)$$

and c_1 and c_0 are the diffusant concentrations at the inner and outer face of the layer (mol cm^{-3}), respectively. Similarly, it is expected that $c'_1 \approx 0$. For the steady state, the producing rate of Li_2O , v_p :

$$v_p = -v_{\text{LiH}} / 2M_{\text{LiH}} = J' \quad (8)$$

and the consuming rate of Li_2O , v_c :

$$v_c = v_{\text{LiOH}} / 2M_{\text{LiOH}} \quad (9)$$

are equal, where v_{LiH} , M_{LiH} , v_{LiOH} and M_{LiOH} are the weight gain rate and the mole mass of LiH and LiOH, respectively. Combining of (6) - (9) yields the ultimate rate equation for the

second stage of LiH hydrolysis:

$$\begin{aligned} m_g(t) &= m_g(t_c) + (v_{\text{LiOH}} + v_{\text{LiH}})(t - t_c) \\ &= m_g(t_c) + \frac{2Dc'_0(M_{\text{LiOH}} - M_{\text{LiH}})}{H_s} (t - t_c) \\ &= Et + F \quad (t > t_c) \end{aligned} \quad (10)$$

where $E = \frac{2Dc'_0(M_{\text{LiOH}} - M_{\text{LiH}})}{H_s}$, $F = m_g(t_c) - \frac{2Dc'_0(M_{\text{LiOH}} - M_{\text{LiH}})}{H_s} t_c$.

To sum up, the rate equation of LiH hydrolysis can be expressed by:

$$m_g(t) = \begin{cases} At^2 + Bt + C & (0 \leq t \leq t_c, \text{parabolic}) \\ Et + F & (t > t_c, \text{linear}) \end{cases} \quad (11)$$

where A, B, C, E and F are constants independent of t. The equation consists of a parabolic stage followed by a linear one, which coordinates with the gravimetric results. The parameters in the equation are related to a few physical properties of the system, such as diffusion coefficient and Li_2O thickness, thus can be used to evaluate these properties indirectly.

D. Li_2O Thickness And Moisture Content Effects

As the rate-determining step is considered to be diffusion through the Li_2O layer, LiH hydrolysis rate can be measured by the diffusion rate in Li_2O . According to the diffusion equation in steady state (Eq. 6), except the constants independent of water concentration, two parameters would affect the flux J' . They are water concentration c'_0 at the interface of surficial LiOH and Li_2O and the steady Li_2O thickness H_s . The relationship can be expressed by $J' \propto c'_0 / H_s$. On the other side, c'_0 is regarded as almost the same as water concentration at the LiOH surface, for the lack of diffusion barrier in the porous LiOH layer [1]. While water concentration at the LiOH surface, depending on the adsorptive properties of LiOH, is approximately proportional to ambient humidity according to Langmuir Equation at very low humidities. As a result, the ultimate hydrolysis rate v_s should be in direct proportion to water concentration of exposure c_w and in reverse proportion to H_s , due to the rate determination of diffusion in Li_2O . This function demonstrates that the Li_2O thickness, other than water concentration of exposure, is another factor that affected the hydrolysis rate.

Both v_s and H_s can be evaluated from gravimetric results by fitting to the rate equation above. v_s can be determined by the slope of the linear stage, E, and H_s can be established by Eq. 7 as well. The fitted results for various humidities were listed in Fig. 2 and Table 1. Table 1 showed that H_s went up as c_w increased. However, the increased H_s , which brought along an extended time for diffusion and thus slowed down the hydrolysis, would impose a negative effect upon v_s . On the other side, the increased c_w , which led to a higher concentration of diffusant and consequently accelerated the hydrolysis, would contrarily impose a positive effect upon v_s . As shown in Table 1, the two totally opposite effects actually led to an upward trend of v_s , which implied that c_w rather than H_s played a predominant role in v_s . The increased rate of LiH hydrolysis at elevated humidities should mostly be attributed to the increased

TABLE I
RATE EQUATION, H_s AND v_s FITTED TO GRAVIMETRIC RESULTS FOR VARIOUS HUMIDITIES

c_w (ppm)	Rate equation	H_s (10^{-5}cm)	v_s ($10^{-7}\text{g}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$)
200	$y = 0.74 \times (x + 22.5)^{1/2} - 3.72$ $0.018x + 3.40$	5.3	1.8
400	$y = 1.11 \times (x + 4.68)^{1/2} - 2.45$ $0.029x + 5.51$	6.6	2.9
700	$y = 1.32 \times (x + 30.5)^{1/2} - 7.38$ $0.085x + 0.04$	7.8	8.5
1200	$y = 2.73 \times (x + 39.9)^{1/2} - 17.6$ $0.120x + 2.73$	11.5	12.0

water concentration instead of the possibly altered Li_2O thickness. This was a little difference from the idea of Haertling, who attributed the increasing of hydrolysis rate to a decreased Li_2O thickness in the moister atmosphere but ignored the effect of increased water concentration. In fact, the accelerated formation of Li_2O at a higher humidity, which had been proved by gravimetric results, may probably lead to a thicker layer of the oxide.

Given that the effects of Li_2O thickness and water concentration of exposure should be both taken into account, an established function derived from Eq. 10 can be concluded as $v_s H_s \propto c_w$, which predicted a direct proportion of $v_s H_s$ to c_w . Fig. 4 depicted $v_s H_s$ as a function of c_w and confirmed the direct proportion. Therefore, this consistency proved that the rate equation based on the model of 'Layer Diffusion Control' was appropriate at least in such low humidities.

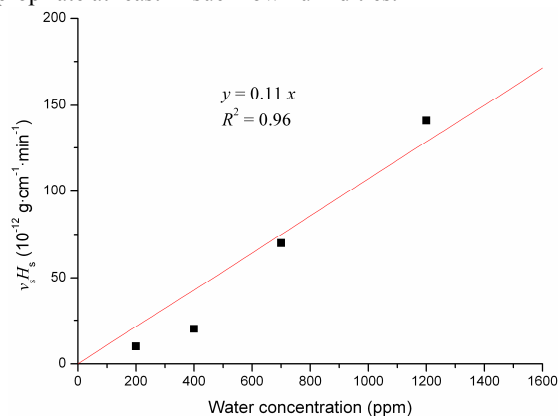


Fig. 4 $v_s H_s$ vs. c_w for different humidities. As predicted by the rate equation, $v_s H_s$ presented a direct proportion to c_w .

IV. CONCLUSION

A combination of gravimetry and Raman spectroscopy was used to obtain insight on LiH hydrolysis kinetics at low humidities of $\text{RH} < 4\%$. The hydrolysis rate derived from gravimetric data established a 'paralinear' behavior and the

critical time for linear conversion was comparable with the time when LiOH appeared in Raman spectra. This comparability was due to the difference in reaction mechanisms as explained by Haertling's model of 'Layer Diffusion Control'.

A two-stage rate equation of Eq. 11 was developed on the basis of 'Layer Diffusion Control' model. The equation was used to quantify Li_2O thickness and to correlate LiH hydrolysis rate with Li_2O thickness and water concentration by fitting the gravimetric data to it. According to the equation, the ultimate hydrolysis rate was affected by both water concentration and the steady Li_2O thickness, and the fitted results presented an increased hydrolysis rate accompanied by a thicker Li_2O layer with water concentration increasing. The totally opposite effects of an increased water concentration and a thicker Li_2O steady thickness actually led to a positive impact on the ultimate hydrolysis rate of LiH, which implied that water concentration, rather than Li_2O thickness, played a predominant role in LiH hydrolysis rate. The increased rate of LiH hydrolysis at elevated humidities should mostly be attributed to the increased water concentration instead of the possibly altered Li_2O thickness. Additionally, the consistency of experimental data and the rate equation validated the 'Layer Diffusion Control' model in the specified conditions.

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