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In situ observation of lithium hydride hydrolysis by DRIFT spectroscopy

Roy P. Awbery [a,*], Duncan A. Broughton [a], S.C. Tsang [b]

[a] *Chemical Technology Division, AWE plc, Reading, Berks RG7 4PR, UK*
[b] *School of Chemistry, Reading University, UK*

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Abstract

Polycrystalline LiH was studied *in situ* using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy to investigate the effect water vapour has on the rate of production of the corrosion products, particularly LiOH. The reaction rate of the formation of surface LiOH was monitored by measurement of the hydroxyl (OH) band at $3676\ \mathrm{cm}^{-1}$. The initial hydrolysis rate of LiH exposed to water vapour at 50% relative humidity was found to be almost two times faster than LiH exposed to water vapour at 2% relative humidity. The hydrolysis rate was shown to be initially very rapid followed by a much slower, almost linear rate. The change in hydrolysis rate was attributed to the formation of a coherent layer of LiOH on the LiH surface. Exposure to lower levels of water vapour appeared to result in the formation of a more coherent corrosion product, resulting in effective passivation of the surface to further attack from water.

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1. Introduction

Lithium hydride (LiH) has a high affinity for water vapour, resulting in a surface layer of lithium hydroxide (LiOH) and/or lithium oxide (Li_2O) on exposure to trace quantities of moisture [1]. Consequently, even though this material is handled under dry atmosphere conditions (~10 ppm H_2O), a surface layer of hydrolysis products can always be detected [2]. LiH is known to continually outgas hydrogen (H_2) due to a solid-state reaction between LiH and LiOH [3,4], but H_2 production is significantly increased during hydrolysis [5,6]. Hydrolysis of the bulk material results in significant swelling due to an increase in molar volume as the LiOH/Li_2O content increases [4,7]. The swelling and production of H_2 has serious implications for fuel storage cells and containment vessels. The swelling can lead to breach of containment and further exposure to moist air and H_2 can lead to hydriding corrosion in reactive metal components. It is therefore important to understand how LiH hydrolysis occurs to be able to predict the extent of hydrolysis under specific conditions of moisture exposure.

Many of the hydrolysis studies on LiH have been conducted under high vacuum conditions and at elevated temperatures. These conditions simplified the studies by removing the added complication of constant and rapid hydrolysis from external water sources. Controlled water vapour dosing was also employed where discreet quantities of water were introduced to the sample prior to monitoring the hydrolysis reactions. However, LiH hydrolysis under ambient conditions has been far less studied [2], and even less so for conditions that are more analogous to those employed for the storage and handling of LiH [8] where constant water vapour exposure can occur. The limited studies under ambient conditions has primarily been due to the difficulty of controlling the reaction environments and because the hydrolysis reactions tend to be very fast.

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* Corresponding author. Tel.: +44 118 982 7020.
E-mail address: roy.p.awbery@awe.co.uk (R.P. Awbery).

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It is probably worthwhile mentioning the difference between the materials used in the studies under ambient and high temperature–high vacuum conditions. In the latter, pure LiH was often used, either as freshly cleaved single crystal or clean polycrystalline solids. Under ambient humidity conditions LiH will not be pure, consisting of a layer of LiOH and/or Li_2O, and it has thus become acceptable to refer to 'Salt' when working with non-pure LiH. For the purposes of this work, ambient humidity conditions refers to the relatively dry conditions LiH would experience within a fuel cell or storage device, i.e. under vacuum or backfilled with an inert dry gas of low water vapour content (0–100 ppm). A comprehensive review of investigative studies into LiH hydrolysis and product decomposition has been carried out independently by Broughton [9] and Haertling et al. [10].

The initial product during LiH hydrolysis is not clear despite three decades of study. The reaction products at elevated temperature and low H_2O partial pressures, and when only monolayer coverage occurs, have been reported [1] to be Li_2O and H_2 (Eq. (1)). At ambient temperature and on exposure to high water vapour concentrations, where more than a single monolayer of H_2O coverage is possible, the products have been reported [1] to be LiOH and H_2 (Eq. (2)). Hydration of LiOH ($LiOH \cdot H_2O$) formed on the surface of LiH has been reported on exposure to excess water vapour [2,7] (Eq. (3)).

$$2LiH + H_2O \rightarrow Li_2O + 2H_2 \tag{1}$$

$$LiH + H_2O \rightarrow LiOH + H_2 \tag{2}$$

$$LiOH + H_2O \rightarrow LiOH \cdot H_2O \tag{3}$$

Both hydrolysis reactions (Eqs. (1) and (2)) are thermodynamically favourable with $\Delta G_{298} = -94\ \mathrm{kJ\ mol^{-1}}$ and $\Delta G_{298} = -133\ \mathrm{kJ\ mol^{-1}}$ for the formation of Li_2O and LiOH, respectively. Several studies have reported that Li_2O forms rapidly as a very thin layer on LiH during hydrolysis (Eq. (1)) [2,11,12] and that Li_2O also reacts rapidly with water vapour to form LiOH (Eq. (4)), where $\Delta G_{298} = -87\ \mathrm{kJ\ mol^{-1}}$.

$$Li_2O + H_2O \rightarrow 2LiOH \tag{4}$$

The decomposition of LiOH, in the presence of LiH, has been studied, mainly under non-ambient conditions [4,7]. LiOH decomposition has been reported to occur in vacuum/dry environments due to the existence of unstable forms of LiOH which was attributed to LiOH near the LiH substrate and ambient interface. Dinh et al. [7] measured a range of activation energies for the decomposition of LiOH, which indicated that LiOH decomposed most easily near the LiH substrate, then near the ambient interface [13]. Dinh's work suggested that stable surface LiOH would also decompose when exposed to a strong water pump at elevated temperature, but at a very slow rate, which is consistent with thermodynamics where the Gibbs free energy for LiOH decomposition is positive $\Delta G_{298} = +174\ \mathrm{kJ\ mol^{-1}}$. Decomposition of surface LiOH may be able to occur under ambient conditions but would require a long time to be observed. Furthermore, the continued presence of H_2O can be expected to shift the equilibrium in favour of LiOH production, thus preventing observation of Li_2O.

This work was part of a wider study [14–19] to investigate the reactions of LiH to provide the data necessary for a predictive ageing model to be developed. The development of such a model requires accurate information on the behaviour of LiH when exposed to known temperatures, pressures and water vapour (or air) exposures. A predictive model is required to support lifetime prediction studies for components or cells fabricated from LiH. Hydrolysis of LiH powder has been studied under variable water vapour exposures at ambient temperature and pressure using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy in order to understand the conditions that promote hydrolysis and the mechanisms involved. Hydrolysis rates were measured by monitoring the growth of LiOH. Li_2O was also selected for investigation because it has been identified as a possible intermediate product during hydrolysis of LiH.

2. Experimental

2.1. Materials

LiH (95% purity), Li_2O (99.5% purity) and LiOH (98% purity) were obtained from Alfa Aesar. KBr (99.99% spectroscopy grade), obtained from Aldrich, was used as the background material for DRIFT spectra and was dried at 400 °C for 24 h prior to use. All samples, including the reference material, were sieved prior to use to produce powders with a particle size range of 53–105 μm. All sample handling and preparation was performed in a dry argon (approx. 10 ppm H_2O) filled glovebox.

2.2. Equipment

DRIFT spectra were recorded using a Perkin Elmer Spectrum 1B FT-IR spectrometer with a medium-band (7800–580 $\mathrm{cm^{-1}}$) MCT detector. The spectrometer was coupled to a variable temperature environmental chamber (Grazeby-Specac Ltd.) and Grazeby-Specac 'Selector' diffuse reflectance mirror assembly. Prior to use, the environmental chamber was purged with dry argon and heated to 500 °C for 24 h to remove residual water vapour from within the chamber. A total of 64 scans per spectrum were continuously recorded, during a period of up to 500 min, over the spectral range 700–4000 $\mathrm{cm^{-1}}$ at a resolution of 8 $\mathrm{cm^{-1}}$ and scanning speed of 1 $\mathrm{cm^{-1}\ s^{-1}}$. This equated to one spectrum collected every 38 s. The background spectra were collected at the same temperature as the DRIFT sample spectra. The background was automatically subtracted from the sample spectra. None of the samples were diluted but total absorbance kept low by utilising a small platinum sample cup (7 mm diameter × 3 mm high) for