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Identification of lithium hydride and its hydrolysis products with neutron imaging

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ABSTRACT

In this study, lithium hydride (LiH) and its hydrolysis products were investigated non-destructively with neutron radiography and neutron computed tomography. Relative neutron transmission intensities (I/I_0) were measured for LiOH, Li_2O and LiH, and their linear attenuation coefficients calculated from this data. We show that ^7Li is necessary for creating large differences in I/I_0 for facile identification of these compounds. The thermal decomposition of LiOH to Li_2O was also observed with neutron radiography. Computed tomography shows that the samples were fairly homogeneous, with very few macroscopic defects. The results shown here demonstrate the feasibility of observing LiH hydrolysis with neutron imaging techniques in real time.

1. Introduction

Lithium hydride (LiH) is a light, hydrogen dense material which has received attention due to its use as a hydrogen storage medium [1–7], whilst its corrosion products, particularly Li_2 O, has been studied as candidate tritium breeding materials for use in commercial nuclear fusion [8–10] and as a electrode material in Li-ion batteries [11]. LiH reacts readily with moisture to irreversibly form surface corrosion layers of Li_2O, LiOH and $LiOH.H_2O$ [12–19]. This poses problems for storage and handling and the material must be kept and processed in vacuum or an ultra-dry inert gas glove box. Even in these conditions, the material slowly hydrolyzes due to trace quantities (less than 1 ppm) of moisture [20,21]. Corrosion layer thickness varies in size and morphology with the environmental conditions [22–24]. On the other hand, controlled LiH hydrolysis has been proposed as an efficient hydrogen generator for portable applications [3,5,6]. Hydrolysis is given by either:

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

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

Alternatively:

$$LiH + H_2O \rightarrow LiOH + H_2 \tag{3}$$

$$LiH + LiOH \rightarrow Li_2O + H_2 \tag{4}$$

In both these reaction schemes, a thin layer of Li_2O forms at the interface between LiH and LiOH. This process is thought to be a diffusion limited process and results in a trilayer LiH–Li_2O–LiOH corrosion system. There is a growing consensus, both experimentally and theoretically, that under ambient conditions, the hydrolysis reaction proceeds via the formation of Li_2O before LiOH (*i.e.* formed by equations (1) and (2)) [12,16,25,26]. In other words, Li_2O is favored by lower moisture exposures and at higher temperatures. At 298 K, the thickness of the Li_2O layer is reported to be in the 10 nm range [16]. Upon heating to 523 K, the conversion of LiOH to Li_2O has been observed on a LiH substrate [14,22,27]:

$$2LiOH \rightarrow Li_2O + H_2O \tag{5}$$

Several analytical techniques have been applied to study these reactions, including infrared spectroscopic methods, x-ray diffraction, gas pressure measurements or thermal decomposition methods. By measuring the –OH resonance, diffuse reflectance

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infrared Fourier transform (DRIFT) spectroscopy has shown the presence of LiOH on the surface of LiH following exposure to moisture. DRIFT spectroscopy has also shown that −OH is lost upon heating, with hydroxide being converted to oxide [14,21,28]. Raman spectroscopy has also been recently applied to the study of LiH corrosion, in particular the measurement of the Li_2O phonon [29–31]. Thermal decomposition and diffraction have provided kinetic and mechanistic information on the hydrolysis of LiH [20] and the subsequent thermal decomposition of the LiOH layer [29–31].

Neutron characterization offers an alternative and as yet unexplored method of probing the nature of LiH and its hydrolysis products. Antecedent studies of LiH with neutrons have, for example, focussed on crystallography [32] and Compton scattering experiments [33]. The use of LiH as a neutron shielding material has also recently been discussed [34]. As opposed to x-ray radiation, neutrons interact strongly with Li and H and thus are attractive as a probe of LiH and its corrosion products. X-ray attenuation is related to the atomic number of the atoms present in a material and therefore LiH is amongst the poorest x-ray absorbers. In the case of neutrons, attenuation is determined by the nuclear structure of a particular atom, with natural Li and H exhibiting very high attenuation characteristics. In this report, neutron radiography and computed tomography (CT) data are obtained for the LiH corrosion system. The main goal of these measurements were to experimentally determine the relative transparencies of LiH, Li_2O and LiOH to cold neutron irradiation. We also wished to observe the thermal dehydration of LiOH with neutron techniques and therefore to evaluate the possibility of imaging LiH corrosion in real time.

2. Experimental

2.1. Materials

Samples were produced from the compaction of powders at ~ 20.7 MPa (3000 psi) in a uniaxial Carver die press using a 6 mm diameter die set. Micron sized LiOH and Li_2O powders were first pressed in laboratory atmosphere, which took approximately 10 min, otherwise they were stored in a dry Ar glove box. The laboratory was maintained at 293 K and had a relative humidity of about 45%. The LiOH/Li_2O sample and the die set were placed in the glovebox, where the LiD powder was loaded. The whole sample was sealed in a polyethylene bag, removed from the glovebox and pressed. At no point was the containment of the polyethylene bag broken, hence the LiD layer was not exposed to laboratory atmosphere. To ensure sufficient neutron transmission, each 6 mm sample was sanded down in the glovebox, by hand, to a thickness of 3 mm parallel to the neutron transmission axis.

Table 1 shows the isotopic composition of the samples used here. The reason for selecting Li compounds enriched with ^{7}Li is two fold. Firstly, samples containing natural Li have sufficient ^{6}Li to prevent any neutron transmission being observable. Secondly, we wish to observe LiH chemistry and thus we are interested in spatial distributions of H and O and therefore variations in attenuation due to Li is not of particular interest; O and H are the mobile species in this system. Instead of using LiH enriched with the ^{7}Li isotope, the decision was made to use Li^{2}H which reduces neutron attenuation via the use of the ^{2}H (D) isotope. We note that the use of ^{7}Li [35] and D [36] in neutron characterization experiments has previously been described. Also the use of D afforded the possibility of observing D mobility in the Li_2O and LiOH layers after thermal treatment. As shown in Table 1, the LiH samples are predominantly ^{2}H and will be referred to henceforth as LiD. Also for brevity 99.99% ^{7}LiOH will be refered to as LiOH. LiD samples were approximately 90% dense compared to the theoretical maximum calculated from x-ray diffraction [16,37]. Li_2O and LiOH both exhibited densities in the region of 95–98% of their theoretical densities [16].

Table 1
Isotopic composition of the samples used in this study. Note that Li_2O (2) was produced via heat treatment of LiOH, see Table 2 for details. Natural O was used in all samples.

Compound	Isotopic Composition (%)			
	^{6}Li	^{7}Li	^{1}H	^{2}H
LiH	7.59	92.41	8	92
LiOH	0.01	99.99	99.99	0.01
Li_2O (1)	2	98		
Li_2O (2)	0.01	99.99		

Table 2
Chemical composition and thermal treatment of samples used in this study. The dimensions given are nominal. The pressure refers to the base pressure during heat treatment. Thermal treatment of LiOH converted it to Li_2O (2).

Sample	Layer thickness (mm) LiD: Li_2O (1): LiOH	Thermal treatment
1	1:0.05:1	673 K, 3 h, 3 Pa
2	1:1:1	
3	powder LiD/LiOH	
4	1:0.16:1	
5	1:0.16:1	673 K, 3 h, 3 Pa

Five samples were produced, four layered and one a mixture of powders. A summary of sample composition, nominal layer thickness and thermal treatment is presented in Table 2. Of the four layered samples, the thickness of the Li_2O layer was varied (0.05 mm and 0.16 mm) to assess its effect on reducing further hydrolysis of the LiD during the thermal decomposition of LiOH (equation (5)). This effect is known to occur in samples containing native corrosion products of LiD, in that further hydrolysis is a diffusion limited process across the Li_2O layer [22,24]. We note that these Li_2O layers are too large to be considered representative of the ambient LiD hydrolysis system but they still have the ability to give useful H_2O transport information across the Li_2 O layer. Thermal treatment was performed *ex-situ* on samples 1 and 5. Samples were removed from the glovebox, wrapped in Al foil before being transported briefly in air to be loaded in an Al vessel. The Al vessel was immediately evacuated to a pressure of approximately 3 Pa. The vessel was placed in a tube furnace and was heated in 100 K increments to a final temperature of 673 K in about 30 min. The temperature was monitored using a K-type thermocouple positioned on the vessel. Pressure increased to 7.4 Pa immediately after the temperature of 673 K was reached and returned to 3 Pa after 45 min at temperature. After 3 h, the furnace was turned off and samples were left in the tube to cool, while maintaining the vacuum.

2.2. Neutron imaging

Neutron radiography was performed using the CG-1D imaging instrument at the High Flux Isotope Reactor, situated within Oak Ridge National Laboratory (ORNL) (Tennessee, USA) [38]. The instrument provides a cold polychromatic neutron beam with a wavelength spread of 0.08–0.6 nm, with an intensity maximum at 0.26 nm. The overall neutron flux is estimated to be 5×10^6 cm^{2}s^{-1}. Neutron radiographs were captured on a LiF/ZnS scintillator attached to a charge coupled device (CCD) camera which has a field of view of 28 × 28 mm^2. The camera was Peltier cooled to about 210 K to reduce thermal noise in the electronics. The resolution of the instrument was determined with a Gd coated grid to be approximately 100 μm. To collect CT data, each sample was rotated through 180° at an increment of 0.17°.