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Novel determination of surface temperature of lithium hydride hydrolysis using DRIFT spectroscopy

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ABSTRACT

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy has been used to show how increasing temperature causes the hydroxyl band of LiOH to shift linearly and reversibly towards lower wavenumbers. The band shift with temperature was used to determine the surface temperature of LiH when exposed to water vapour at 158, 317, 793 and >1900 Pa (5%, 10%, 25% and >60% relative humidity), the exothermic hydrolysis reaction resulting in surface temperature increases of up to 50 °C. The rate of surface heating was found to increase slightly with increasing water vapour exposures up to 793 Pa, demonstrating that the LiH hydrolysis reaction rate was dependent upon the partial pressure of water vapour. The growth of surface LiOH appeared to significantly slow down further reaction until the water vapour exposure was increased beyond 1900 Pa, when formation of hydrated LiOH occurred. The effect of temperature on detectors was also investigated showing that baselines shifted towards higher intensities with increasing temperature when measured with a DTGS detector and towards lower intensities with an MCT detector, over the temperature range 25–450 °C.

1. Introduction

Lithium hydride (LiH) has been identified as a suitable material for use as a neutron shield in nuclear reactors due to its high hydrogen density and also as a potential hydrogen fuel source due to its low weight density. LiH has also been investigated as a potential tritium breeding material for use in fusion reactors. In all of these applications LiH will need to be contained or encapsulated in some form. Therefore, the long-term stability of this material needs to be understood in terms of the environmental exposures it is likely to encounter throughout its production cycle.

Lithium hydride (LiH) has a high affinity for water vapour, hydrolysing quickly to form a surface layer of predominantly lithium hydroxide (LiOH) with the evolution of hydrogen gas [1]. Consequently, even when LiH is handled under ultra dry atmosphere conditions (~1 ppm H_2O) a surface layer of LiOH can always be detected [2]. The growth of surface LiOH can lead to significant swelling or spalling due to the increase in molar volume as the LiOH content increases [3,4]. This swelling can potentially have serious implications for fuel storage cells and containment vessels as it can result in breach of containment. Furthermore, the evolution of H_2 from the hydrolysis of LiH 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.

Previous studies of LiH hydrolysis have tended to concentrate on elevated temperatures and high vacuum conditions using thermogravimetry [1] and pressure rise measurements [3–6]. Studies at ambient temperature have included diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy [7–10] but were aimed at identification and quantification of surface LiOH. Water vapour exposure has also been investigated during the DRIFT studies, with the aim of determining hydrolysis reaction mechanisms and kinetic data [9]. However, the hydrolysis of LiH is very exothermic and it was considered that this could potentially lead to significant localised heating of the sample surface, which in turn may affect the obtained DRIFT spectra.

Variable-temperature DRIFT (VT-DRIFT) spectroscopy is ideally suited to the investigation of reaction kinetics and to studies of solid-state changes caused by heating [11–15], provided that the effect of temperature on the spectrometer detector is known. It has been reported [12] that DRIFT spectra baselines can shift with temperature when measured using a (photoconductive) mercury–cadmium–telluride (MCT) detector. Furthermore, it has been reported that elevated temperatures lead to expansion of the sample [16,17], particularly the surface, resulting in the IR beam no longer being focussed correctly on the sample surface. The defocused IR beam resulted in variations in, or shifting, of spectral band intensity, width and frequency. This problem was reportedly overcome [12] by using a DRIFT accessory adapted to include a sample stage that was mounted upon a screw thread, allowing the relative height of the sample to be adjusted. Altering the sample height allowed the IR beam to be correctly focussed at all times, despite

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surface movement on heating. It was noted that this method was not ideal because the sample surface would move during rotation of the screw thread, resulting in a different part of the sample being exposed to the IR beam and potentially leading to problems with spectral reproducibility. This method was shown to be suitable for reducing baseline shifts for temperatures up to 200 °C, although they are not completely removed. Equally, the need to record background spectra at the same temperature as the sample has been recognised [17] along with the need to ensure that the sample temperature has equilibrated before spectra are obtained.

Modern DRIFT accessories now typically allow the mirrors, which direct and focus the IR beam to and from the sample surface, to be adjusted rather than the sample itself. This method prevents any movement of the sample in the beam and enables in situ measurements of DRIFT spectra using fully enclosed environmental chambers, fitted with infrared transparent windows. However, the difference between MCT and the less sensitive (pyro-electric) deuterated triglycine sulphate (DTGS) detectors has not been clearly identified in terms of the effect temperature can have on baselines, band shape and position.

This work aimed to understand how temperature variations could affect the relative response of DTGS and MCT detectors, and how the detector response affected both background baseline and the position of bands associated with the hydrolysis of LiH when exposed to water vapour at 158, 317, 793 and >1900 Pa (5%, 10%, 25% and >60% relative humidity). This information was important to ongoing efforts to utilise DRIFT spectroscopy to obtain quantitative and kinetic data on the formation of LiOH during LiH hydrolysis. This work was part of a wider study [6–9,18,19] 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). A predictive model is required to support lifetime prediction studies for components or fuel storage cells fabricated from LiH.

2. Experimental

2.1. Materials

LiH (99% 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 milled for 3 min using an IKA A11 grinding mill and sieved prior to use to isolate powders with particle size less than 38 μm. The powder samples (30 mg) were loaded into a platinum cup (7 mm diameter × 3 mm high) prior to placing inside the variable temperature environmental chamber (Grazeby-Specac Ltd.). All sample handling and preparation was performed in a dry-argon (approximately 1 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 cm^{-1}) MCT detector and a DTGS detector. The spectrometer and environmental chamber was coupled to a Grazeby-Specac 'Selector' diffuse reflectance mirror assembly. The IR beam focus could be adjusted by movement of the upper focussing mirrors using a micrometer screw. Focussing was achieved by moving the mirrors until the interferogram centre-burst showed maximum signal. 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 30 scans were recorded per spectrum over the spectral range 4000–700 cm^{-1} at a resolution of 4 cm^{-1} for both MCT and DTGS detectors. A background spectrum was collected at the same temperature as the DRIFT sample spectra over the range 25–450 °C and the background subtracted from the sample spectra. Total absorbance was kept low by minimising the amount of sample analysed by placing in a platinum sample cup, which was placed directly into the environmental chamber sample cell.

DRIFT spectra have been presented as percent reflectance, which is analogous to transmission used in classical infrared spectroscopy. Background baseline measurements were taken at 1910 cm^{-1} and hydroxyl bands were measured using the O–H stretching mode located at 3676 cm^{-1} at ambient temperature.

3. Results and discussion

3.1. Detector response to elevated temperatures

3.1.1. DTGS detector

To examine how sample temperature can influence the baseline signal in DRIFT spectra obtained using a DTGS detector, the environmental chamber was loaded with dry KBr and the spectrometer interferogram monitored for total radiation throughput (detector response in counts) over the temperature range 25–450 °C. The detector response was measured both by leaving the IR beam focus unaltered to show how the response changed with temperature, and with the focus adjusted. The adjustment was to maintain the same detector response at elevated temperatures as that observed at 25 °C.

With the IR beam focus adjusted to maintain the same detector response throughout heating of the KBr background sample, it was found that very little adjustment of the mirrors was necessary. A single spectrum was recorded at 25, 100, 200, 300, 400 and 450 °C and when plotted together showed slight shifting of the baseline towards higher signal intensity (Fig. 1).

By contrast, when the KBr sample was heated without adjustment of the mirrors (Fig. 2) the baseline was observed to shift significantly towards higher intensities. Overall, the baseline shifted by 3.7% when the mirrors were adjusted to give a nearly constant detector response. With no adjustment of the mirrors to compensate for heating and sample expansion the baseline shifted by 20.4%. However, it should be noted that the overall baseline shift even without mirror adjustment, was still relatively small; approximately 0.13 arbitrary units between that observed at 25 °C and that at 450 °C.

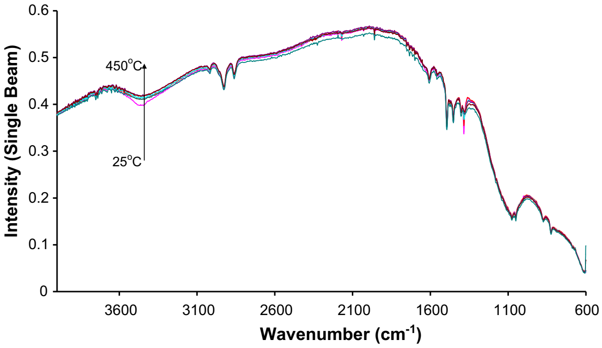

Fig. 1. Single beam spectra of KBr observed with a DTGS detector with IR beam focus adjusted to maintain the same detector response at all temperatures, showing the baseline shift slightly towards higher intensity with heating.