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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.

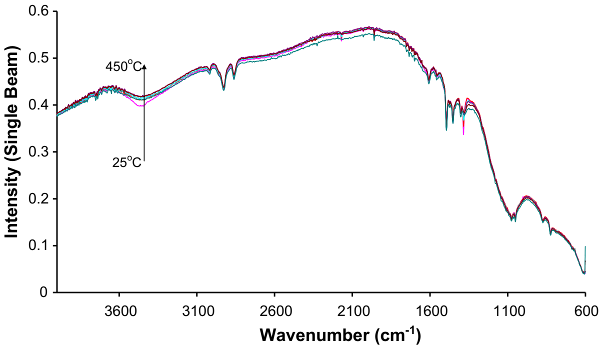

Fig. 1. Single beam spectra of KBr observed with a DTGS detector with IR beam focus adjusted to maintain the same detector response at all temperatures, showing the baseline shift slightly towards higher intensity with heating.

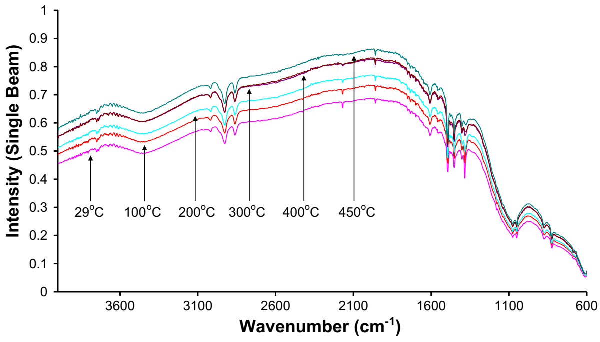

Fig. 2. Single beam spectra of KBr observed with a DTGS detector without adjustment of the IR beam focus, showing more pronounced baseline shift towards higher intensity on heating.

Fig. 3 shows that the background baseline shifted in concert with the detector response, demonstrating that baseline intensity was directly related to the amount of radiation reaching the DTGS detector. In Fig. 3 the triangles (▲) denote values of detector response and baseline intensity when the IR beam focus was adjusted on heating, squares (□) denote values when the IR beam focus was adjusted on cooling and circles (●) denote baseline intensity and detector response values when the IR beam focus was not adjusted on heating. The shifting was clearly more pronounced when the IR beam focus was not adjusted during heating. This trend demonstrated that the infrared radiation emitted from the sample during heating was readily detected and therefore should be considered when conducting quantitative work at temperatures above ambient. However, the infrared throughput to a DTGS detector, when coupled with an environmental chamber with zinc selenide windows, is very low and the use of MCT detectors has become more commonplace. MCT detectors are photoconductive devices and operate in a different manner to the pyroelectric DTGS detectors and therefore, their response to temperature changes was also investigated. However, DTGS detectors are still invaluable for long-term observations where the need for constant liquid-nitrogen filling can be avoided and where non-air sensitive materials are studied.

3.1.2. MCT detector

KBr spectra were measured over the range 25–400 °C using an MCT detector, with the IR beam focus adjusted to maintain the same detector response at elevated temperatures as that observed at 25 °C (Fig. 4). In Fig. 4 the triangles (▲) represent baseline intensity values, whilst squares (■) represent the detector response values. Solid lines show the response to increasing temperature and dashed lines show the measured responses to baseline intensity and detector response on cooling from 400 °C down to 25 °C.

The IR beam focus was successfully adjusted to maintain a response of approximately 440 counts up to 200 °C, after which it was not possible to adjust the focus to maintain the same response. The detector response reduced and was accompanied by a reduction in the baseline intensity; the converse of the DTGS detector, where values increased on heating. On cooling the sample, the baseline and detector response moved back again to increased detector response and baseline intensity. The variation on heating and cooling was not linear and, unlike the DTGS detector, the values reached on cooling were not the same as those measured on heating despite attempting to adjust the beam focus; some hysteresis was evident between 200 and 400 °C (Fig. 4). The baseline signal on heating and cooling varied by 9.6% and 19.8%, respectively.

Background spectra from KBr were again collected over the temperature range 25–400 °C, this time without adjustment of the IR beam focus during heating. The baseline shifted significantly towards lower intensity (again the converse of the DTGS detector) and was followed by a significant reduction in the detector response from 200 °C onwards (Fig. 5). Triangles (▲) denote baseline intensity values, whilst squares (■) denote detector response values. Solid lines represent increasing temperature and dashed lines represent decreasing temperature. No hysteresis was observed when the IR beam focus was unaltered on heating. Furthermore, the detector response and baseline intensity returned to approximately the same values for each temperature, regardless of how many times the sample was heated and cooled. Without adjustment of the beam focus the baseline shifted by 40.4% on heating and 38.4% on cooling.

The difference between the detector response and the baseline shift of the DTGS and MCT detector suggested that thermal expansion of the sample surface was not solely responsible for baseline artefacts in DRIFT spectra. The results indicated that the detectors were also responsible for the differences in response. It has been suggested [16] that on heating there is an increased amount of unmodulated infrared radiation emitted from the sample, and MCT detectors are unable to measure this. Unmodulated radiation has been suggested to effectively dilute the modulated IR signal reaching the MCT detector, resulting in reduced detector response. By contrast, the DTGS detector appeared to be able to detect the increased infrared radiation emitted from the heated sample.

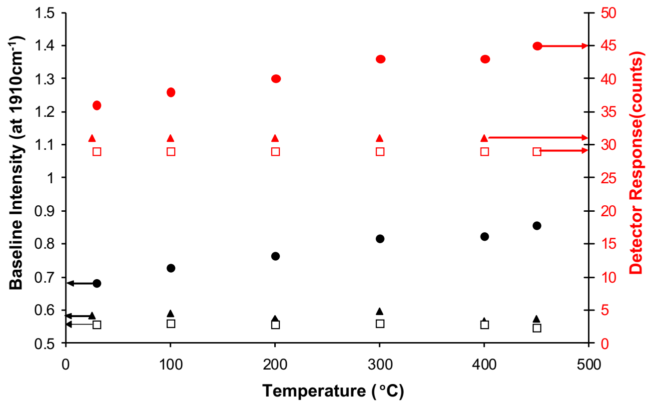

Fig. 3. DTGS detector response (red markers) and KBr baseline intensity (black markers) shown to be in concert with each other, both on heating with IR beam adjustment (▲)and on cooling without IR beam adjustment (□) and on heating without IR beam adjustment (●). The arrows indicate the relevant ordinate scale.

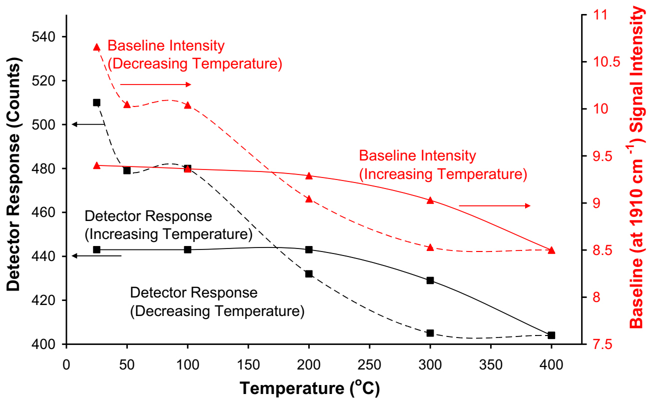

Fig. 4. Plot of MCT detector and KBr baseline response to varying temperature, with IR beam focus adjusted, demonstrating the relationship between detector response and baseline intensity. Triangles (▲) denote baseline intensity values, whilst squares (■) denote detector response values. Solid lines represent increasing temperature and dashed lines represent decreasing temperature.

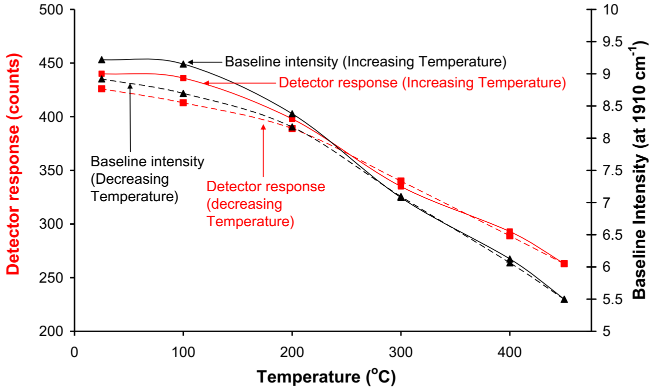

Fig. 5. Plot of MCT detector response (■) and KBr baseline response (▲) to temperature, with the IR beam focus unaltered during heating, showing that on heating (solid lines)and cooling (dashed lines) the baseline and detector response shifts reversibly in concert with each other.

3.2. Hydroxyl band shifting in LiOH on LiH

Fig. 6 shows a typical, undiluted, LiH DRIFT spectrum. A strong, broad band was observed at 1300 cm^{-1} attributable to Li–H. Evidence of water vapour exposure is shown by the appearance of the hydroxyl band associated with O–H stretch in LiOH at 3676 cm^{-1}.

DRIFT spectra of LiH powder (particle grain size less than 53 μm), were obtained after water vapour exposure, over the range 25–400 °C using an MCT detector, without IR beam adjustment. The hydroxyl band shifted towards lower wavenumbers on heating, reaching 3667 cm^{-1} at 400 °C, a shift of 11 cm^{-1} and also increased in width (Fig. 7). On cooling to room temperature the hydroxyl band shifted back to its original position and the band narrowed again. The Li–H band was not observed to shift. The hydroxyl band shifting was also observed with a DTGS detector over the same temperature range.

Fig. 8 shows the OH band shifting with temperature as observed with an MCT detector. It was not clear what was responsible for the observed hysteresis. However, the detector response was also found to exhibit hysteresis when plotted against temperature, suggesting that the detector was being affected by heating and directly affecting the resultant spectra. Furthermore, when the hydroxyl band shift was measured using a DTGS detector the response was again linear but hysteresis was not observed, suggesting that the hysteresis effect was only observable with the MCT detector and may therefore have been an artefact of the detector itself rather than the sample.

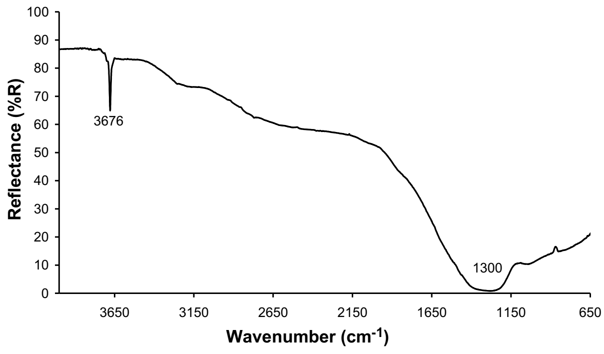

Fig. 6. Typical DRIFT spectra of LiH showing evidence of water vapour exposure with the OH peak at 3676 cm^{-1}, attributed to formation of LiOH.

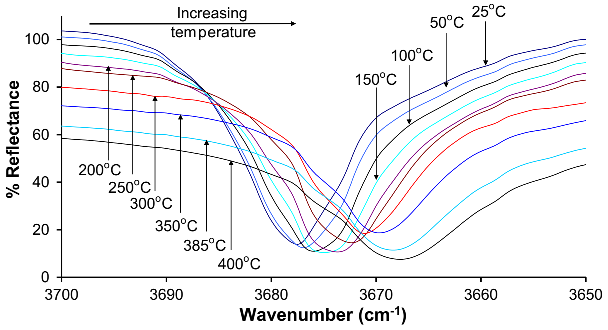

Fig. 7. DRIFT spectra of LiH powder measured over 25–400 °C, after water vapour exposure, showing reversible shifting of the OH band towards lower wavenumbers and broadening of the bands on heating.

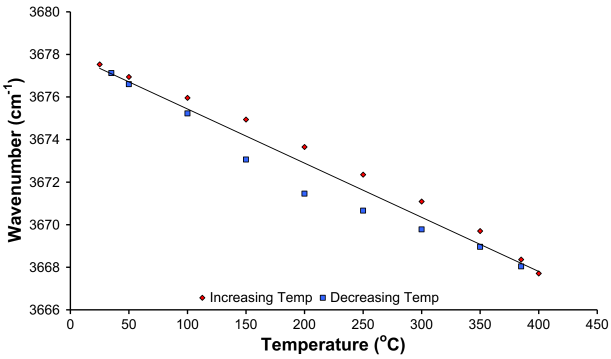

Fig. 8. Reversible hydroxyl band shifting with varying temperature observed with LiOH formed at the surface of hydrolysed LiH using an MCT detector.

To determine whether the band shifting was due in part to the presence of LiOH formed on the surface of another material, for example LiH or Li_2O, the effect of temperature on pure LiOH was also investigated. The position of the hydroxyl band was measured after allowing the temperature at each point to equilibrate, again without adjustment of the IR beam focus. The band shifting, on heating and cooling, was observed to be linear when measured using an MCT detector (Fig. 9). The band shift observed with the DTGS detector was almost identical to that of the MCT detector and is therefore not shown. There was no evidence of any hysteresis in the pure LiOH spectra measured with the MCT detector, suggesting that the MCT detector was able to detect an effect arising from surface LiOH that the DTGS detector could not. Therefore, the observed hysteresis in the hydrolysed LiH samples may be an indication of different bonding of OH at the surface to that nor-

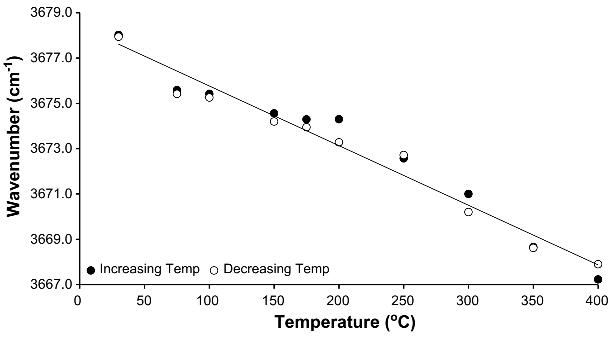

Fig. 9. Hydroxyl band in pure LiOH shifting towards lower wavenumbers on heating and back again on cooling, as observed with an MCT detector.

mally observed in bulk LiOH, although it was not understood why the OH band position should vary for the same temperature on heating and cooling.

DRIFT has been used previously to identify and quantify the presence of LiOH on LiH by measurement of the hydroxyl stretching band at 3676 cm^{-1} [20]. Tanaka et al. [21] reported measurement of the OH band in hydrolysed samples of Li_2O and noted that the band shifted towards lower wavenumbers, and became broader, on heating. They attributed this behaviour to a change in interaction among the hydroxyl species: at room temperature the surface comprises mostly coherent LiOH, but at higher temperatures LiOH begins to decompose leaving –OH adsorbed on the surface of LiOH. However, this would be expected to produce at least two bands representing the two different environments of the hydroxyl species; that in the pure LiOH phase and that adsorbed onto the Li_2O surface. In practice, only one OH band was observed by Tanaka, which shifts with temperature. Furthermore, it seems unlikely that all of the OH that exists in LiOH will be converted to OH adsorbed on the surface of Li_2O. If such conversion were occurring, a mixed phase of both LiOH and Li_2O might be expected, at least until conversion of the surface species was complete. It is proposed that the increase in temperature may alone be responsible for the band shift and broadening due to thermal excitation causing increased lattice vibration and reduction in sample density. As the bond vibrates on heating the average bond length will increase, and therefore become weaker resulting in the band moving to lower wavenumbers. On heating, the relative flexibility of the lattice will increase resulting in the average bond lengths becoming less uniform causing a broadening of the observed vibrational bands.

3.3. Calibration

The hydrolysis of LiH is exothermic and previous work [7] had shown evidence of slight movement of the hydroxyl band at the onset of hydrolysis observed at ambient temperature. Given the linear and reversible band shifting reported previously, the shift observed at ambient temperature may be indicative of surface heating caused by the exothermic hydrolysis reaction. Therefore, it was considered that a calibration factor for the OH band shift with temperature could be obtained and used to determine the extent of surface heating during hydrolysis.

A calibration graph was produced by measuring the hydroxyl band shift over the temperature range 25–125 °C. This range was chosen to confirm that the calibration factor was reproducible and linear over the lower temperature range of interest. The slope was 0.026 cm^{-1} °C^{-1} with a correlation coefficient of 0.9979, which compared well with the values obtained previously from the powdered samples. The hydroxyl band shift values were divided by the calibration factor to determine the surface temperature of the samples during exposure to water vapour.

3.4. Surface temperature determination of LiH hydrolysis

3.4.1. LiH powder at 5%, 10% and 25%RH exposure

LiH powder (30 mg), with particle grain size of less than 53 μm, was loaded into the DRIFT cell under an argon atmosphere (<1 ppm H_2O). Five replicate samples were exposed to a moist flow of argon each at 5%, 10% and 25%RH (158, 317 and 793 Pa, respectively) at a flow rate of 100 cm^3 min^{-1}.

At 5%RH exposure the OH band was observed to shift by an average of 0.87 cm^{-1} in 1.96 min (Fig. 10), or 0.23 °C min^{-1}. After 40 min of water vapour exposure the OH band had not shifted back to its original position, and remained 0.43 cm^{-1} below the origin, suggesting that the sample remained warmer than before the onset of hydrolysis.

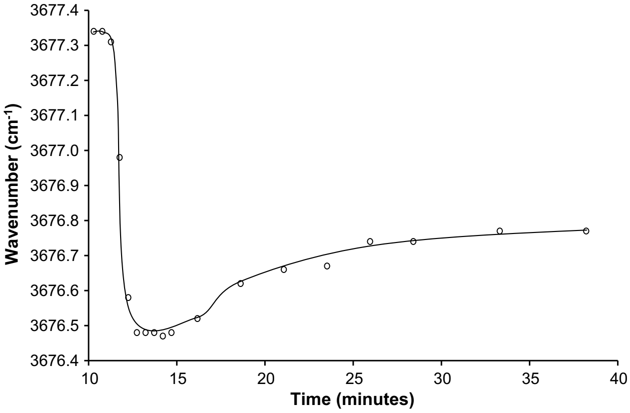

Fig. 10. Hydroxyl band shift observed in powdered LiH on exposure to 5%RH (158 Pa) water vapour, indicating the rapid increase in surface temperature, by up to 33.1 °C, as hydrolysis proceeded until a thickening layer of LiOH formed, resulting in less heat generation.

The band shift appeared to represent a calculated temperature increase at the surface of 33.1 °C. It should be noted also that there was a lag of 2 min before the OH band started to move. The timescale on the plots run from 10 min due to the spectrometer being set up to collect spectra before water vapour dosing, which was after 10 min. It was not clear why there was a 2 min lag before the band was observed to shift, but was considered to be due to formation of sufficient LiOH to be detectable or possibly due to the initial formation of Li_2O before further hydrolysis to LiOH. DRIFT spectra were unable to show positive indication of the presence of Li_2O.

At 10%RH (317 Pa) the OH band shifted by 1.39 cm^{-1} in 3.43 min (Fig. 11), over an average of five separate samples. The band shift correlated with a calculated temperature increase of 53.5 °C. The rate of band shift, and hence temperature increase, was higher than that observed at 5%RH (158 Pa) at 0.30 °C min^{-1}. Again, there was a time lag before the LiOH band was observed to shift towards lower wavenumbers, of approximately 3 min. As with the 5%RH (158 Pa) exposure, the OH band was not observed to shift back to its original position prior to exposure. After 40 min the band appeared to have reached its final position, which was 0.20 cm^{-1} below its origin.

At 25%RH (792 Pa) water vapour exposure the OH band (Fig. 12) was observed to shift by 1.28 cm^{-1} in 2.46 min, a rate of 0.33 °C min^{-1}. The band shift correlated with a temperature change of 49.2 °C. During exposure the OH band did not shift back

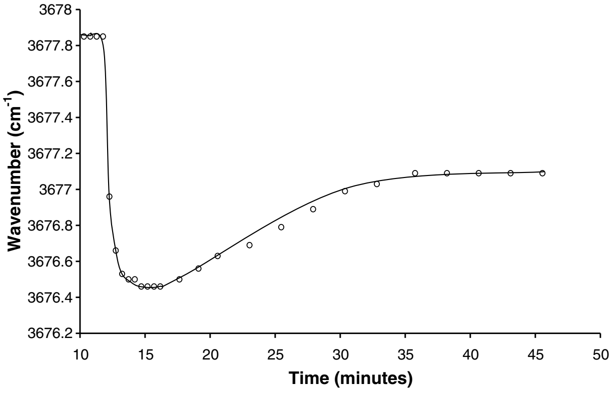

Fig. 11. Hydroxyl band shift observed in powdered LiH on exposure to 10%RH (317 Pa) water vapour, representing a temperature increase of 53.5 °C.

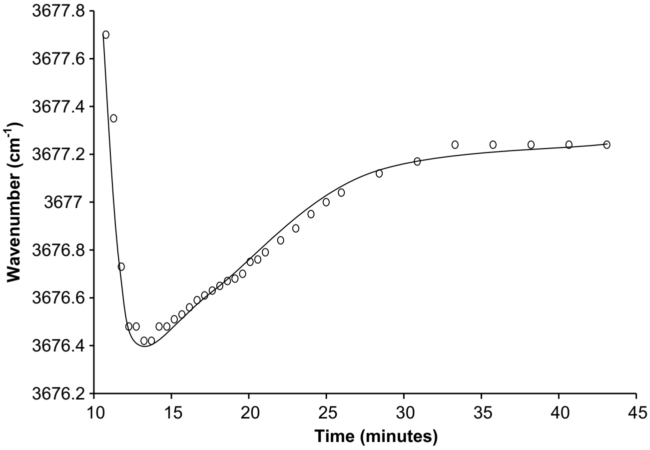

Fig. 12. Hydroxyl band shift observed in powdered LiH on exposure to 25% RH (792 Pa) water vapour, indicating a surface temperature change of 49.2 °C.

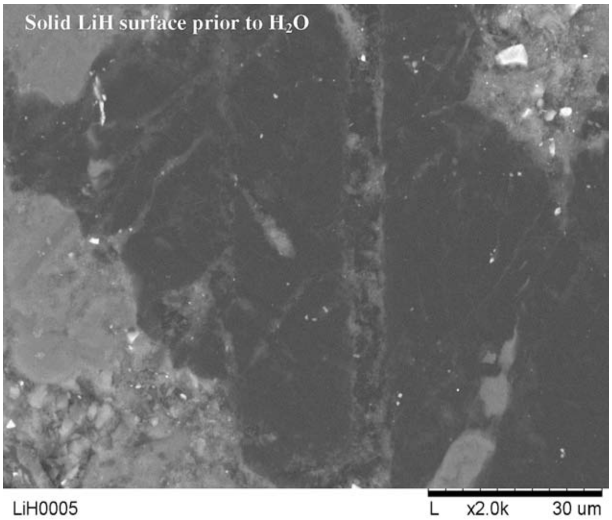

Fig. 13. SEM images of a pressed LiH surface before water vapour exposure showing relatively clean surface with grain boundaries evident.

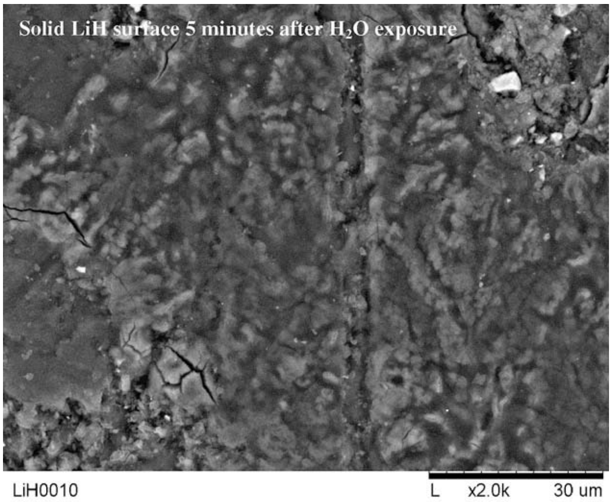

Fig. 14. SEM images of a pressed LiH after water vapour exposure of 5 min showing formation of cracks and fissures as LiOH forms across the surface.

to its origin, remaining 0.46 cm^{-1} below, again suggesting that the sample remained warmer than prior to water vapour exposure.

The OH peak height continued to increase throughout the water vapour exposures, but the band was observed to stop moving to lower wavenumbers and began to gradually shift back to higher wavenumbers after approximately 13 min. The observed increase in OH peak height indicated continued growth of LiOH. The initially rapid shift to lower wavenumber was attributed to surface heating from the exothermic hydrolysis reaction until a surface layer of LiOH had built up. The LiOH layer was considered to effectively passivate the surface resulting in significantly slower reaction with water vapour and hence less heat generation, resulting in the troughs observed in Figs. 10–12. The continued hydrolysis of the sample would then be dependent upon diffusion of water (or $-OH^-$) through the ever increasing layer of LiOH at the surface. However, LiOH continued to grow due to the formation of cracks and fissures at the surface, due to lattice mismatch, at the LiH surface as LiOH is formed. The continued growth of LiOH below the surface resulted in continued surface heating, albeit to a much lesser extent due, in part, to heat transfer losses through the thickening layer of LiOH. SEM images of a solid disc of LiH, taken before water vapour exposure (Fig. 13) and 5 min after (Fig. 14) clearly show the formation of these cracks and fissures. A solid disc of LiH was used to illustrate more clearly the formation of these cracks and fissures.

Table 1 summarizes the band shift values for each exposure of LiH powder to water vapour; the values quoted are an average of five repeat experiments at each exposure level. Increasing the water vapour concentration resulted in a slight increase in the rate of hydroxyl band shift and therefore an increase in the rate of temperature change on hydrolysis. The total time for the hydroxyl band to shift to its lowest position was similar for all water vapour exposures up to 25%RH (793 Pa), approximately 2.5 min, with only the extent of band shifting changing. The rate of band shift for each level of water vapour exposure up to 25%RH (793 Pa) was relatively constant (Fig. 15) and the rate of band shift was observed to increase slightly with increased water vapour exposure.

3.4.2. LiH powder at 60%RH exposure

On exposure to more than 60% RH (>1900 Pa) water vapour the OH band shifted by 0.25 cm^{-1} in 2.45 min (Fig. 16), which corre-

Table 1
Summary of band shift data and temperature changes during hydrolysis of powdered LiH exposed to water vapour

Water vapour exposure (RH)	OH band shift (cm^{-1})	Band shift duration (min)	OH band shift rate (cm^{-1} min^{-1})	Calculated temperature change (°C)	Rate of temperature change (°C s^{-1})
5% (158 Pa)	0.86	2.41	0.35	33.1	0.23
10% (317 Pa)	1.39	2.94	0.47	53.5	0.30
25% (792 Pa)	1.28	2.46	0.52	49.2	0.33
>60% (1901 Pa)	0.25	2.94	0.085	9.6[a]	–

[a] *Note*. The calculated temperature change for water vapour exposure above 60%RH appears much lower due to the formation of $LiOH \cdot H_2O$, resulting in severe sample swelling and therefore gross errors in band position and intensity.

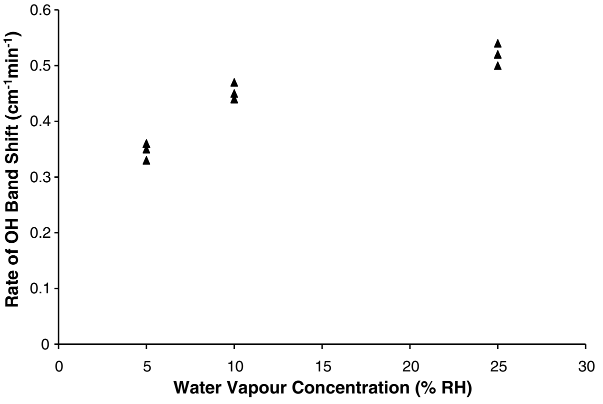

Fig. 15. Comparison of rate of hydroxyl band shift as a function of water vapour exposure to powdered LiH, showing that the rates were relatively constant at each level of exposure.

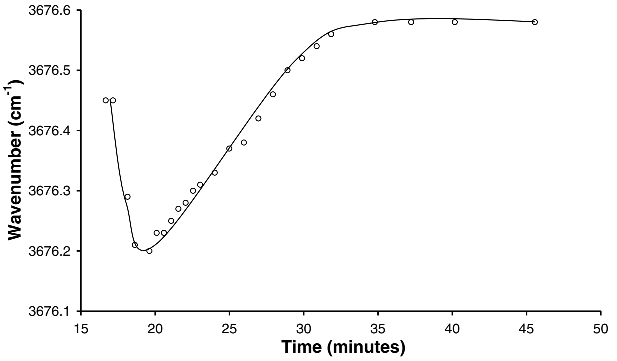

Fig. 16. Hydroxyl band shift observed in powdered LiH on exposure to more than 60%RH (1900 Pa) water vapour.

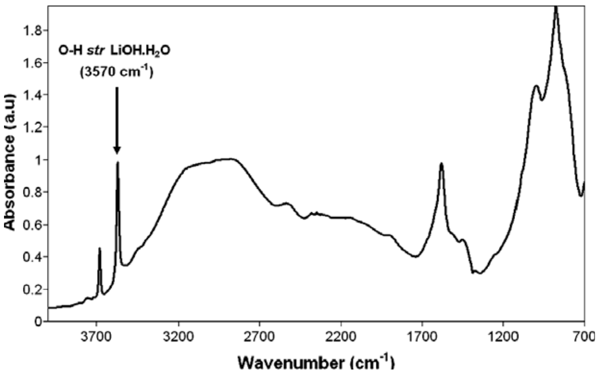

Fig. 17. DRIFT spectra of LiH after exposure to water vapour in excess of 60%RH, showing the formation of $LiOH \cdot H_2O$ with the appearance the OH band at 3570 cm^{-1} accompanied by broad hydrogen-bonded band from 3500–2700 cm^{-1}.

lated to an apparent temperature increase of 9.61 °C, significantly lower than the values obtained at lower levels of exposure. The DRIFT spectra showed evidence of not only LiOH but also formation of $LiOH \cdot H_2O$, as shown by the appearance of an additional O–H band at 3570 cm^{-1} along with a broad band from 3500 to 2700 cm^{-1} attributable to H-bonded OH (Fig. 17).

The formation of $LiOH \cdot H_2O$ was not observed during exposures to water vapour below 60%RH and its formation resulted in the powder sample swelling and spalling at the surface. Consequently, the sample swelling led to the IR beam no longer being focussed on the true sample surface and resulted in inaccurate measurement of the OH band. Monitoring of the OH band indicated there was a less significant band shift on water vapour exposure and unlike the lower exposures, the band shifted back to a higher wavenumber than it originally started from. The differing OH band shift behaviours were attributed to interference by the monohydrate band at 3570 cm^{-1} to the signal intensity and position of the OH band at 3676 cm^{-1}. Upon evacuation the bands associated with $LiOH \cdot H_2O$ disappeared resulting in the OH band returning back to its original position, thereby confirming that the monohydrate bands were adversely affecting the OH band measurements at 3676 cm^{-1}.

4. Conclusions

The temperature stability of both DTGS and MCT detectors when used to obtain DRIFT spectra at elevated temperatures has been determined. Both detectors were found to be affected by increased temperature, with the DTGS detector resulting in baseline shifts towards higher intensities and the MCT detector shifting the baseline of background spectra towards lower intensities. The baseline shift was considered to be the result of unmodulated infrared radiation emitted from the sample surface resulting in increased IR signal in the DTGS detector. A decreased signal was observed with the MCT detector due to the way the detector only counts modulated radiation; the unmodulated IR input from the heated sample was effectively diluting the overall signal to the MCT detector.

This work has shown that when using a fully enclosed environmental chamber an MCT detector, with its increased sensitivity, is the preferred detector for working at low light levels. However, it has been demonstrated that the MCT detector is significantly affected by unmodulated infrared radiation being emitted from the sample on heating. The DTGS detector was relatively unaffected and it was easier to adjust the IR beam focus to maintain the same radiation throughput. The need to obtain background spectra at the same temperature as the sample spectra for IR work conducted at elevated temperatures has been highlighted.

Increasing temperatures were shown to cause the hydroxyl band of LiOH to shift towards lower wavenumbers. The shift was found to be completely reversible and linear for both DTGS and MCT detectors enabling the calibration of hydroxyl band position with temperature. The calibration was used to determine the local surface temperature of LiH when exposed to water vapour, the exothermic 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 60% RH (1900 Pa), when LiOH formation was replaced with formation of hydrated LiOH.

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