Experimental investigation on lithium hydride hydrolysis

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\textbf{ABSTRACT:}

In order to have a better understanding of LiH reaction with water, several experimental techniques were investigated and tested to determine whether they were suitable or not in a kinetic purpose. Among them, Raman spectroscopy and X-Ray photoelectrons spectroscopy (XPS) gave particularly interesting results and are extensively used in the field of our kinetic and phenomenological study of H\textsubscript{2} production by LiH hydrolysis.

\textbf{KEYWORDS:} Raman spectroscopy, XPS, decomposable hydride, lithium.

1- Introduction:

Lithium and lithium-base components have many issues especially in the field of energy. Moreover, lithium hydride (LiH) is, among solid materials, one of the most efficient neutron absorber and the lighter one. But LiH is a chemically decomposable metal hydride as well, and is therefore an attractive candidate for H\textsubscript{2} storage and delivery applications. It provides indeed the highest density form of hydrogen storage with a maximum capacity approaching 2,000 cm\textsuperscript{3} TPN/cm\textsuperscript{3} (if LiH theoretical density is assumed).

However, because of its potential hydrogen content, LiH is also a hazardous material which requires special attention for industrial handling. It reacts instantaneously and violently with water, manipulations and conditioning must therefore be operated under dry and inert glove-box atmosphere, and, in case of long time storage, H\textsubscript{2} released is feared, resulting from a reaction between LiH and either H\textsubscript{2}O trace-level, or its hydrolysis product LiOH.

LiH hydrolysis may result from several reactions which principal ones are summarized in Figure 1.

\begin{center}
\includegraphics[width=\textwidth]{figure1.png}
\end{center}

\textbf{Figure 1 :} The major reactions between LiH and water

Numerous research groups, using various experimental methods and apparatus, as described in a recent review from Haertling et al. [1], have investigated LiH hydrolysis. Nevertheless, these studies generally exhibited contradictory conclusions regarding reaction schemes and even the species involved. For instance, the role of lithium oxide Li\textsubscript{2}O is not clearly established. Moreover, contribution of diffusion processes in the
apparent reaction rate is sometimes evoked [2,3] but the competition between chemical and transport phenomena had never been extensively studied.

We therefore intended a phenomenological study of LiH reaction with water, whose ultimate objective is the development of a predictive model for hydrogen production (or prevention) in a wide range of operating conditions. Prior to this investigation, appropriate experimental methods were tested.

2- Investigation strategy:

To be suitable for a phenomenological investigation, an experimental method must be at the same time:

- selective: each of the species involved should have its own and specific signature
- quantitative (and accurate): signals intensity should be related to the amount of reactants and/or products
- quick enough to allow a real time detection
- and it should allow an accurate control of the sample environment, especially if a highly reactive constituent such as LiH is involved.

Mainly because the latter requirement is particularly difficult to fit, it appears while reviewing investigations on LiH hydrolysis that many methods were used without offering all these criteria simultaneously [1]. Indeed, the reaction between LiH and water has been studied:

- either in a straightforward way considering a freshly cleaved single crystal submitted to a beam of water molecules (for instance MBMS [4]), under vacuum conditions, or consecutive to a given water-exposure (by SEM observations [3,4]), thus not allowing identification of the reaction products, unless afterward analysis are processed;
- or using indirect methods, which offer more freedom regarding sample size and morphology (crystal, powder, pellets) as well as its environment. From such methods, many information relative either to the reaction product identification (for instance TPD [5]) or to the apparent reaction rate (such as gravimetric [4]) can be obtained, but not both.

Among the characterisation methods available, X-ray Photoelectron Spectroscopy (XPS) and Raman Spectroscopy (RS) had never been mentioned (and thus, probably used) within studies of LiH hydrolysis. However, it seems that an experimental investigation involving these two techniques could offer an interesting combination of the required particularities. Indeed (i) the overall introduction circuit of the XPS unit is enclosed in a controlled-atmosphere glove box, thus preventing the sample from pollution outside the UHV chamber; (ii) Raman spectroscopic measurements can be made in situ, providing the controlled-atmosphere sample holder is equipped with a laser-transparent window. Combining both methods can therefore be particularly relevant for the purpose of a simultaneous phenomenological and kinetic study of LiH hydrolysis. Hence, RS is sufficiently “macroscopic” to study the influence of parameters such as sample morphology, reactants concentration and/or flow-rate, temperature, etc. Conversely, XPS could help investigating interfacial phenomena: from the sample initial (residual) oxidation level up to the very first steps of the hydrolysis process.

On the one hand, the selectivity of Raman spectroscopy was evaluated. In this aim, all the species mentioned in Figure 1 have been supplied and investigated. Then we checked whether the method sensitivity and response-time were compatible with the real-time detection of an air-exposed LiH sample evolution.

On the other hand, the feasibility of LiH analysis by XPS was investigated. The major uncertainties regarding this method are deriving from the material behavior (metal hydride, low atomic number) under XPS operating conditions (ultra-high vacuum, electrons removal).

3- Equipments:

Raman spectroscopy measurements have been recorded with a T64000 Jobin Yvon apparatus, equipped with a mixed Ar and Kr ion laser for excitation and with an Olympus BX40 optical microscope. Experiments have usually been carried out at room temperature with the 458 or 514 nm laser line. No noticeable difference was observed between these two wavelengths. Samples of oxidized species were simply deposited in a ceramic crucible, whereas lithium hydride was enclosed in a quartz tube, prepared and sealed within a dry atmosphere glove box (assuring an H$_2$O content lower than 40 vppm). A TS1500 Linkham heating stage was used for high temperature experiments.

An “as received” from Acros Organics single crystal of lithium deuteride (LiD) was used for XPS investigations (Figure 2) and the effect of Ar ions sputtering at the crystal surface has been investigated.
Experiments were performed within an ESCALAB 200i (Vacuum Generator) using a AlKα X-Ray source at 1486.6 eV. The introduction device is located in a controlled atmosphere glove box (this device is especially dedicated to radioactive materials). The measurement chamber pressure remained below 10⁻⁸ Pa during the experiments.

**Figure 2**: View of the ESCALAB apparatus (left side) and of the positioned LiD sample (right side)

4- Raman spectroscopy results:

Although, to the best of our knowledge, Raman spectroscopy has never been used to study the kinetic of LiH hydrolysis, Raman measurements on ⁶LiH, ⁷LiH and ⁷LiD [6], ⁶LiOH, ⁷LiOH, ⁶LiOD and ⁷LiOD [7], LiOH,H₂O [8] and β-Li₂O [9] have already been reported. No Raman measurements on the unstable α-Li₂O phase could been found. Table 1 summarizes the position of the main Raman peaks of some of these compounds relevant to the present study.

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**Table 1**: Position in cm⁻¹ of the main Raman lines taken from [6-10]
We started by recording, at room temperature, the Raman spectra of Li$_2$O (Aldrich), LiOH,H$_2$O and LiH (both supplied by Acros Organics) polycrystalline powders. These experimental results agree with the previously mentioned papers. However, the commercial Li$_2$O powder was found to contain a small amount of LiOH. In order to obtain pure LiOH and pure Li$_2$O, the LiOH,H$_2$O and Li$_2$O powders have been respectively heated. Heating Li$_2$O allowed us to confirm the results obtained in [9] showing a frequency shift and a broadening of the Raman line of Li$_2$O with increasing temperatures.

As can be seen in Table 1, the low-frequencies signatures of LiOH, LiOH,H$_2$O and Li$_2$O are quite different. Moreover, the Raman signals are intense enough to allow monitoring while formation of small amounts of the latter phases. Because there is no first order Raman signal for LiH, the Raman signature of this crystal comes from second order scattering only and is therefore rather weak and composed of broad bands. This allows observation of small amount of hydrolysis reaction's products which could have been masked by an intense first order Raman signal. Therefore, a LiH powder was studied during the hydrolysis step. The powder was hermetically enclosed inside a quartz tube and we monitored the Raman signal after the tube was opened and the powder exposed to ambient air (see Figure 3).

No particular attention was paid to operating conditions (H$_2$O concentration, exact temperature, etc.). Hence, the conclusions that can be derived from these raw experiments (aimed at calibrating the methods parameters like: acquisition time, amplifying modes, etc), are not relevant for a rigorous kinetic investigation. However, results obtained during this feasibility study indicate the apparition of LiOH within the sample, with no evidence of Li$_2$O formation.

![Figure 3: Raman spectra of LiH inside the quartz tube (bottom curve) and after ambient air exposure (middle curve). The top spectrum was obtained for LiOH.](image)

Despite these promising preliminary results, there are some drawbacks to this approach. First, as was observed on our LiOH,H$_2$O powder and reported on LiH [6], an additional background signal due to photoluminescence makes it sometimes difficult to record the Raman signal. Another issue revealed by these preliminary tests is that under air exposure, we could monitor the formation of Li$_2$CO$_3$, probably due to the reaction of LiOH with ambient CO$_2$. The observed Raman lines correspond to the one reported by Brooker and Bates [10] which are given in Table 1. Li$_2$CO$_3$ formation was observed after long-time air exposures and also while heating LiOH,H$_2$O. Figure 4 shows the spectra recorded on a LiD crystal after a 20-hours air exposure. The Li$_2$CO$_3$ Raman lines and the photoluminescence background are so intense that no other Raman signature can be seen in this frequency range.
A different way to handle this problem without being affected by either photoluminescence or formation of lithium carbonate, is to focus on the OH stretching frequency domain. Of course, this prevents from monitoring Li$_2$O formation. The suitability of this approach was only tested during the in-situ transformation of LiOH,H$_2$O to LiOH when heating. Figure 5 presents measurements on LiOH,H$_2$O at room temperature and at 100°C. The sample was heated at 10°C/min and was kept at this temperature. Spectra have been recorded at different times and clearly show the slow conversion as the 3566 cm$^{-1}$ peak which is characteristic of LiOH,H$_2$O vanishes while the intensity of the 3663 cm$^{-1}$ peak of LiOH increases.

Using this approach, it was indeed possible to record the OH stretching Raman signal in the LiD sample exposed to air during 20 hours. This spectrum reveals the presence of both LiOH and LiOH,H$_2$O.

An other interesting feature was observed while studying the LiOH,H$_2$O spectrum evolution with temperature. An undefined (but reproducible) spectrum was indeed recorded at 590°C while investigating the low frequency region (Figure 6). Unlike the Li$_2$O spectrum, recorded on the powder heated at 750°C, which is persistent after sample cooling, the Raman signal measured around 665 cm$^{-1}$ on the powder heated at 590°C is temporary, thus revealing the unstable nature of the involved specie, and thus preventing us from collecting and analysing it.

Investigations are still in progress in order to determine if this peak, which is not inventoried in Table 1 could be attributed to the $\alpha$-Li$_2$O phase described by Machin [2].
5- XPS results:

As previously indicated, there are two kinds of uncertainties regarding XPS analysis of lithium hydride. The former is associated to the ultra high vacuum conditions prevailing during the experiment. Indeed, besides its very low hydrogen equilibrium pressure at room temperature, hydrogen desorption, which will compromise the analysis, cannot be fully excluded, especially from powder. To overcome this first difficulty, we decided to investigate a LiD single crystal sample (LiH crystals were not available). The second problem is associated to the experimental procedure itself. The method is indeed based on the analysis of electrons removed from the sample, under X-Ray induction, but only four electrons are present in the primitive shell of LiH. An important charge of the sample is therefore expected, which will also compromise the results interpretation. A similar phenomenon was already observed in Li$_2$O XPS studies [11].

![Figure 7: XPS spectra of LiD (gene) and Li(1s), O(1s) and C(1s) spectra in the sample](image)

The results of the LiD crystal analysis are given in Figure 7. First, no noticeable outgassing of the sample has been observed. Moreover, the analysis results are confirming that the sample actually undergoes a non-negligible charge during the analysis, but this phenomenon induces a constant shift of the spectra (from 9 to 14 eV), which is therefore compatible with an exhaustive inventory of the surface species (providing an adequate calibration).
Even if special attention has been paid for the sample introduction, C and O-containing species were observed at the sample surface. This contamination, presumably Li₂CO₃ and LiOH or Li₂O, may therefore be attributed to the crystal elaboration process. However, both C(1s) and O(1s) signals intensity decrease after a short ionic abrasion of the sample as illustrated in Figure 8.

Figure 8: C(1s) signal evolution with ionic abrasion (evidence for surface pollution)

This first set of XPS experiments has demonstrated the compatibility of XPS for lithium hydride analysis purpose. However, XPS relevance in the field of a kinetic study is still not straightforward considering the material reactivity (and that, even if pollution sources were minimized in this study) together with the extreme sensitivity of the method.

6- Conclusions:

Raman spectroscopy (RS) and X-Ray photoelectrons spectroscopy (XPS) have been investigated and exhibited particularly interesting results, regarding the study of LiH hydrolysis process:
- each of the involved species has been characterized using RS and in each case an individual evidence or signature has been defined and validated whether by thermal (TGA/TDA) or structural (X-Ray diffraction) analysis;
- and LiH revealed sufficient compatibility with the XPS investigation operating conditions.

Furthermore, response-time and sensibility of Raman spectroscopy measurements appeared to be suitable for kinetic purpose. In this aim, a specific sample holder, dedicated to controlled-atmosphere RS measurements, and allowing the LiH hydrolysis process to be investigated either under “batch” or “gas flow” conditions, has been conceived and is currently under fabrication.

To conclude, Raman spectroscopy and XPS are particularly relevant for a phenomenological and kinetic study of LiH hydrolysis. Combining these methods allow a large range of operating conditions to be explored. For instance, water vapor concentration going from trace level (where XPS seems to be particularly attractive) up to partial pressure enabling H₂ production level compatible with a battery supply (Raman spectroscopy) will be investigated, and the competition between reaction and transport phenomena will be studied.

References:


