Laboratory studies of H retention and LiH formation in liquid lithium

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highlights

- Absorption and thermal desorption experiments of hydrogen isotopes in liquid lithium have been performed at exposure temperatures up to 400 °C.
- The kinetics of the involved processes indicate a two-stage mechanism for hydride production.
- TDS peaks at temperatures well below the expected one for thermal decomposition of the hydride were systematically recorded, although only a small fraction of the absorbed gas was released during the TDS cycle.
- The absorption of H_2 in a D_2-loaded sample was investigated at two temperatures, and no obvious influence of the preexisting species in the rate of absorption of H_2 was seen.
- Deuterium absorption takes place at a higher rate than that of hydrogen.

article info

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abstract

Laboratory experiments on H/D retention on liquid lithium followed by thermal desorption spectrometry (TDS) have been performed at Ciemat. Two different experimental set ups were used in order to expose liquid Li to hydrogen gas or to hydrogen glow discharge plasmas at temperatures up to 673 K. In the present work the results concerning the gas phase absorption are addressed. Two different kinetics of absorption were identified from the time evolution of the uptake. Alternate exposures to H_2 and D_2 were carried out in order to study the isotope exchange and its possible use for tritium retention control in Fusion Reactor. Although important differences were found in the absorption kinetics of both species, the total retention seems to be governed by the total sum of hydrogenic isotopes, and only small differences were found in the corresponding TDS spectra, on which evidence of some isotope exchange is observed. The results are discussed in relation to the potential use of liquid lithium walls in a Fusion Reactor.

1. Introduction

The use of lithium as a PFC in a future reactor is, among other factors, compromised by the well-known tendency to form hydrides, of direct impact on the tritium inventory control imposed by the nuclear safety regulations [1]. Although several studies on gas–lithium and plasma–lithium interaction have been published in the last decade, the complexity of the system makes it difficult to assess how a hypothetical molten lithium element exposed to a divertor plasma would behave. Quantitative particle balance studies are only available for divertor plasma simulator studies and, although some studies have addressed the effect of total fluence on the hydride formation yield [2], no similar records exist respect to the effect of impinging energy of the plasma particles. This point becomes relevant for realistic plasma scenarios in the presence of ELMs, when simultaneous presence of low and high-energy ions impact in the target. Therefore, it is important to check if gas phase and plasma exposure of liquid lithium surfaces lead to the same phenomenology. Studies on gas and plasma exposure (with hundreds of eV plasma particles) including the uptake and the TDS characteristics are presently addressed at Ciemat, although only gas exposure absorption and the posterior desorption (TDS) results of H_2 in lithium, performed at two different temperatures (473 K and 673 K), are reported in the present work. These results are compared with bibliographic data from gas and plasma exposures.

Even if lithium hydride is readily formed, regardless of the form on which H is present, efforts to remove tritium from a potential tritium containing lithium by thermal desorption or isotope exchange are valuable. In that respect, no studies on isotope exchange on

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molten lithium surfaces have been found in the literature. Here we present H_2 absorption and desorption studies in liquid lithium with D_2 pre-absorbed. The detection of HD gives some evidence of isotope exchange. The effect of the pre-absorption of D_2 atoms in the H_2 absorption and desorption from Lithium is also addressed.

2. Experimental setup

The experiments are performed in the set-up shown in Fig. 1. It consists of a cylindrical SS glow discharge chamber (Chamber 1), which is used for the plasma experiments and an adjacent, 2 l smaller chamber (Chamber 2) in which the H_2 and D_2 absorption and desorption experiments are carried out. As mentioned above, only the results of the gas phase adsorption are addressed in this work and Chamber 1 was only used for gas storage.

The oven (Fig. 1, Oven 2) consists of a 3 cm diameter SS cylinder heated by a thermocoax, and it is charged with 3 g of fresh lithium and inserted into Chamber 2. Prior to absorption experiments, heating the sample up to 823 K is systematically performed for conditioning purposes. After that, Chamber 1 is filled to around 33 kPa H_2 pressure and then, the valve connecting it to Chamber 2 is opened and immediately closed, so the pressure drop in Chamber 2 due to the H_2 absorption can be monitored over time with no extra pumping. In order to take into account the effect of the heating of the H_2 gas in the monitored pressure for the case of 473 K and 673 K absorption experiments, blank experiments (heating of the oven without lithium) were performed and the pressure drop during the absorption experiments was corrected accordingly. The quantity of absorbed H over time can be calculated from the corrected pressure drop in Chamber 2 and its volume.

After the absorption experiment for each of the studied temperatures, the valve separating the two chambers is opened and the remaining H_2 gas is pumped away. In order to measure the H_2 desorption, TDS cycles are performed up to 823 K. A Quadrupole Mass Spectrometer (QMS) is used to measure the H_2 (mass 2) and several other signals, and the shutter between the QMS and the oven is closed to prevent the possible contamination of the filament for the highest temperatures due to lithium evaporation. The QMS H_2 signal is absolutely calibrated prior to the experiments.

For the case of D_2 pre-absorption experiments a similar procedure was followed. The oven is recharged with 3 g of fresh lithium and cleaned up to 823 K. Afterwards Chamber 1 is filled to around 13 kPa of D_2 and then, the valve connecting it to Chamber 2 is opened and immediately closed, so the pressure drop in Chamber 2 due to the D_2 absorption can be monitored over time. When the desired D_2 amount has been absorbed, the valve is opened and the remaining D_2 gas is pumped away before proceeding to the H_2 exposure, which is carried out exactly in the same manner as before except that for this case the initial filling pressure is 13 kPa. Two different temperatures were studied in this case, 473 K and 673 K. The total amount of D_2 pre-absorbed in clean lithium at 473 K was 2.8×10^{-3} mol (1.33% D_{mol}/Li_{mol}). At 673 K the amount was 1.0×10^{-2} D_2 moles (corresponding to 4.7% D_{mol}/Li_{mol}).

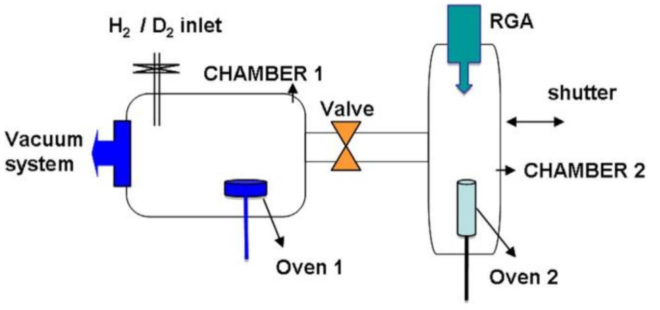

Fig. 1. Experimental set-up.

After each absorption experiment a TDS was performed to measure the H_2, D_2 and HD desorbed amounts. Once again the quadruple H_2 and D_2 signals are absolutely calibrated prior to the experiments. The HD signal was not absolutely calibrated and a sensitivity equal to that of H_2 was assumed.

3. Results and discussion

3.1. *H_2 gas absorption and desorption experiments in lithium*

Fig. 2 shows the corrected H_2 pressure drop over time during the absorption experiments in lithium for the two studied temperatures 473 K and 673 K. The pressure drop of H_2 over time shows a clear two-phase absorption for both temperatures; a fast absorption followed by a more slow absorption that shows a linear dependence with time (independent of the working pressure). Due to the relatively low values of absorbed gas vs. the initial filling amount, a linear behaviour would be expected for first order kinetics, as deduced in previous works. The first phase is related to the absorption of H_2 forming a solution of dissolved hydrogen in lithium, a phase. When the solubility limit is reached [3–5] no further hydrogen can be dissolved and a second absorption phase takes place, where the excess hydrogen would eventually form precipitates of polycrystalline LiH, 1 phase, which cannot be seen with our set-up. The values of the % hydrogen absorbed (% H_{mol}/Li_{mol}) in the first phase obtained in the present study (0.3% and 1.1% at 473 K and 673 K, respectively) are in good agreement with literature values of saturated H solubility in Li [6] for the case of 673 K (1.2%) but are higher than literature values for 473 K (0.043% and 0.31% at 473 K and 573 K, respectively). When absorption at 673 K was continued for several hours, reaching a total of 20% H_{mol}/Li_{mol}, no signs of saturation were observed and even at this high composition, the absorption rate remained unaltered.

The 2nd phase absorption rate constant (K_r), (deduced from the $\ln(P/P_o)$ vs. time plot [7] omitting the first minutes and divided for the exposed Li area) increase with increases temperature (7.14×10^{-7} and $7.14 \times 10^{-6}\,s^{-1}\,cm^{-2}$ at 473 K and 673 K, respectively).

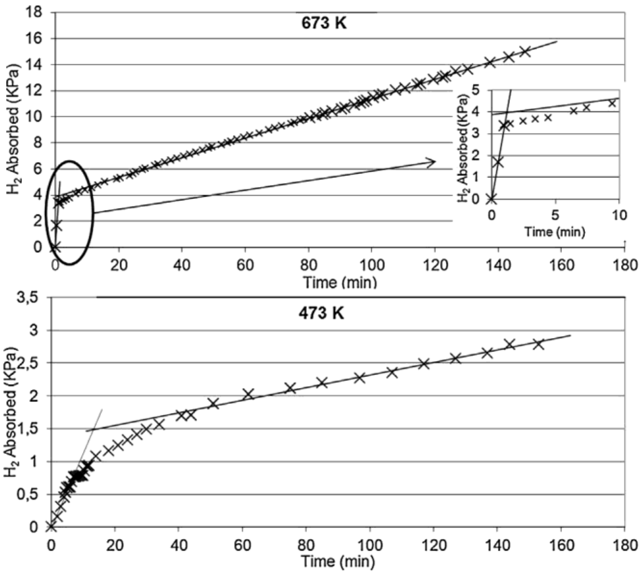

Fig. 2. Corrected H_2 pressure drop over time during the H_2 absorption experiments in lithium for the two studied temperatures, 473 K and 673 K. Solid lines represent the linear fitting to the two observed absorption phases.

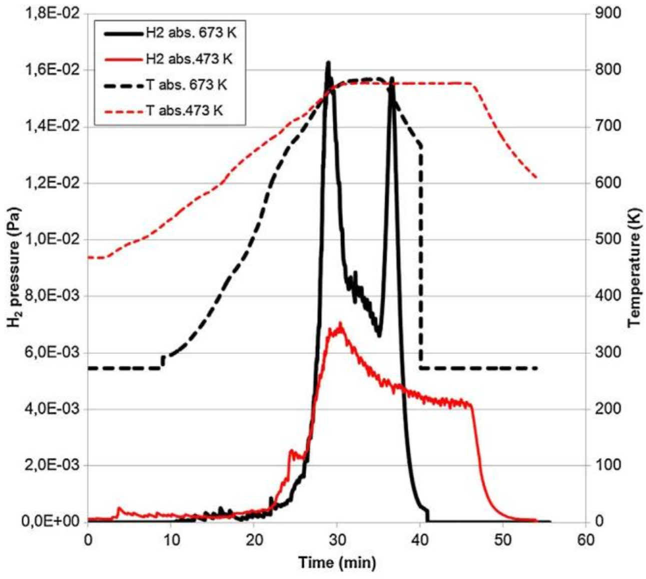

Fig. 3. H_2 thermal desorption spectra up to 773 K for the two different studied H_2 absorption temperatures, 473 K and 673 K.

Assuming a simple Arrhenius functionality for the rate constant, $K = A \times \exp(-E_a/kT)$, activation energy of 0.3 eV for the 1 phase, is deduced, in good agreement also with previous reports [7].

Fig. 3 shows the H_2 thermal desorption spectra up to 773 K for the two different absorption temperature cases. There is a clear desorption peak around 758 K for both cases. Similar peaks have been previously reported from plasma exposed and gas exposed liquid lithium experiments [8,9]. This temperature is clearly lower than the decomposition temperature of LiH and is related to the desorption of hydrogen dissolved in the a phase. Nevertheless, the total amount of desorbed hydrogen calculated from the data is only about a 10% of the total amount of hydrogen in the saturated a phase for the case of 673 K absorption, pointing to an important role of diffusion, perhaps followed by hydride formation during the heating process. If it is so, it would imply the reverse of the assumed displacement of the precipitate phase to produce the decomposition of the hydride within a liquid lithium solution proposed in the literature [9]. Therefore more work is required to properly close the H balance under the desorption phase.

For the case of 473 K absorption, after the peak desorption a pressure plateau is reached at constant temperature (500 °C). A similar result would be expected if the TDS for the case of 673 K absorption would have been kept longer at 773 K so that an equilibrium could have been achieved. For the case of 473 K absorption, the value of the plateau pressure is around 4 mPa, which corresponds to the decomposition pressure of LiH at 813 K [10]. This value of pressure at constant temperature is characteristic of a a + 1 phase equilibrium and has been previously observed for the case of deuterium absorption [9]; the hydrogen gas pressure (decomposition pressure) in contact with the mixture is constant at a constant temperature, as indicating a phase transition. That is, an attempt to increase or decrease the gas pressure isothermally, simply results in positive or negative gas consumption by the molten mixture to produce a corresponding change in the amount of the precipitate phase with the gas pressure remaining unaltered. In a desorption situation, where the conditions are kept close to equilibrium, hydrogen desorption occurs in a similar manner. During this period, precipitated 1 phase dissolves into the surrounding liquid a phase, consequently maintaining the level of a phase deuterium at the solubility limit, while the a phase loses deuterium to the gas phase.

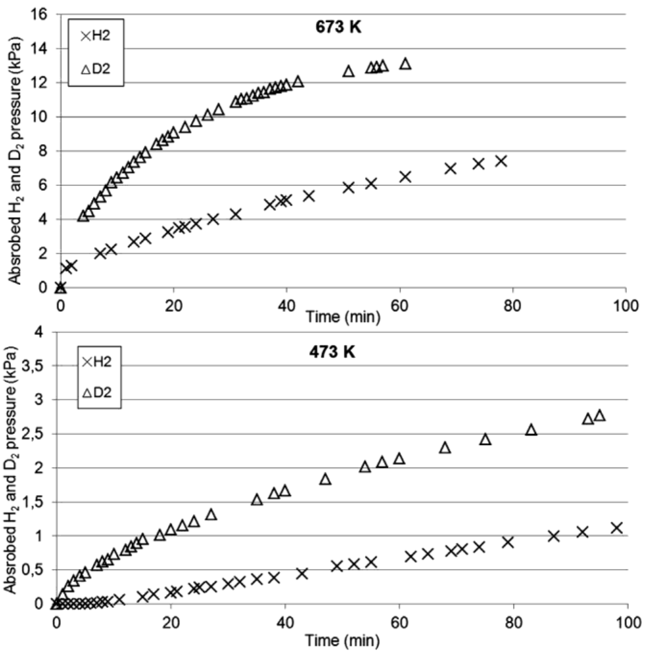

Fig. 4. Corrected H_2 and D_2 pressure drop over time during the H_2 and D_2 absorption experiments in lithium for the two studied temperatures, 473 K and 673 K.

For the case of 673 K we observe a peak in the cooling down phase from 773 K to 673 K. This behaviour has also been seen in other similar experiments [2], it is attributed to the decrease in solubility when lowering the temperature and the consequent release of H_2 retained in the solution. The fact that the same peak is not observed in the 473 K case can be related to the fact that for this case the equilibrium has been already reached.

3.2. Hydrogen absorption and desorption experiments in lithium with deuterium pre-absorption

A pre-absorption of D_2 in clean lithium before the absorption of H_2 was performed at 200 °C and 673 K (Li/D sample). After the absorption of H_2 in Li/D sample (Fig. 4), the TDS study was performed (Fig. 5).

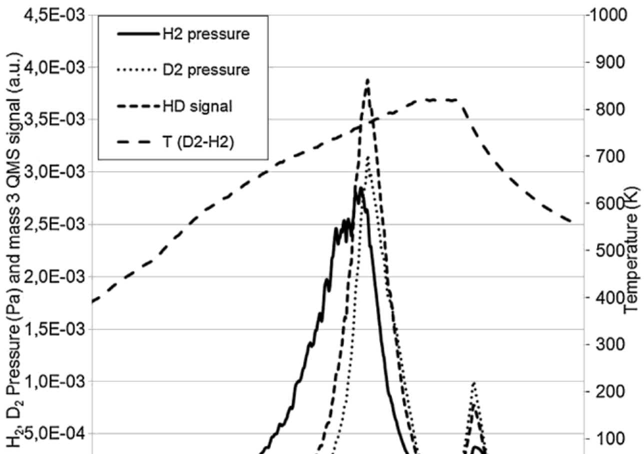

Fig. 5. H_2, D_2 and HD thermal desorption spectra up to 773 K for the experiment of H_2 absorption at 673 K with D_2 pre-absorption.

Table 1
Constants rates (K_r) and activation energy (E_a) for the H_2 or D_2 2nd absorption phase when are absorbed in clean Li or in Li/D sample.

Sample	Absorbed gas	K_r at 200 °C (s^{-1} cm^{-2})	K_r at 400 °C (s^{-1} cm^{-2})	E_a (eV)
Clean Li	H_2	7.14×10^{-7}	7.14×10^{-6}	0.32
	D_2	4.05×10^{-6}	1.22×10^{-4}	0.47
Li/D sample	H_2	2.38×10^{-6}	2.14×10^{-5}	0.30

3.2.1. Absorption of D_2 and H_2

Fig. 4 shows the temperature corrected pressure drops over time in the chamber due to the absorption of D_2 and H_2 in clean lithium and in Li/D sample, respectively, for the studied temperatures, 473 K and 673 K.

As can be seen from Fig. 4, the two phases that were present when H_2 is absorbed in clean lithium (Fig. 2 solid line, Section 3.1), are also visible when the absorption of D_2 in clean lithium takes place, but they are not so easily distinguishable when H_2 was absorbed on Li/D sample, where almost no first phase is observed. In the case of absorption at 473 K the amount of H_2 absorbed on Li/D sample in the first phase is much less than the amount absorbed on clean Li. At 673 K there is not 1st phase absorption of H_2 at all when it takes place in the Li/D sample. That suggests that somehow the D_2 pre-absorbed fully accounts for the first phase of the absorption.

The 2nd phase absorption rate constants (K_r), as well as the 2nd phase activation energies (E_a) for D_2 and H_2 absorption on liquid lithium are showed in Table 1.

The data show that the temperature of the sample during the absorption process has some effect in K_r values, these being lower at lower temperature. The K_r in the case of the absorption in clean Lithium is lower for H_2 absorption than for D_2 absorption, independently of the absorption temperature. The pre-absorption of D_2 increase the value of the K_r of the subsequent H_2 absorption process.

It is difficult to compare the obtained K_r values to those found in literature (Gardner [7] 9.4×10^{-4}, 673 K; Parry [11] 1.4×10^{-7}, 568 K) due to the different experimental conditions and the scarcity of points in the Arrhenius plot and its associated errors. Nevertheless we observed that our K_r values are in between the K_r values obtained in these previous works [7,11].

Regarding the calculated activation energies (E_a) the 2nd phase absorption process in clean lithium is higher for D_2 absorption than for H_2 absorption and no effect of the D_2 preabsorption in Li is observed in the E_a of the subsequent H_2 absorption process as it is deduced from the similar values of the E_a of the H_2 2nd phase absorption in Li/D sample and the H_2 2nd phase absorption in clean Li.

3.2.2. TDS study

Fig. 5 shows the H_2, D_2 and HD thermal desorption spectra up to 773 K for the case of 673 K absorption. The peak temperature agrees with the previous experiments (around 758 K). H_2 desorption is observed to start at lower temperatures than D_2 and the peak temperature of D_2 desorption is a somewhat higher, what would be in agreement with the more favourable formation of LiD in comparison with LiH. Interestingly the total amount of H + D moles desorbed in the peaks is very similar to the total amount of desorbed H moles in the previous case, about a 10% of the saturated quantity and similar H_2, D_2 and HD quantities are observed.

Perhaps the most direct implication of the results here presented to the potential operation of a liquid lithium based reactor is the fact that not only the plasma, but the simple exposure of the lithium elements to neutral gas counts for the total inventory of H isotopes on the reactor walls. In principle this fact could open the possibility to isotope selective removal by exposure to the non-radioactive isotopes, H_2 and D_2 of the T-containing elements. Due to the small quantities of absorbed gas recovered during the TDS cycles at $T < 823$ K, strategies aimed at decomposing the corresponding hydrides at temperatures compatible with a reactor operation still remain to be developed. More work in this line is presently in progress in CIEMAT.

4. Conclusions

Absorption and thermal desorption experiments of hydrogen isotopes in liquid lithium have been performed at exposure temperatures up to 673 K. The kinetics of the involved processes has been investigated and a two-stage mechanism for hydride production was deduced and characterized. TDS peaks at temperatures well below the expected one for thermal decomposition of the hydride were systematically recorded, although only a small fraction of the absorbed gas was released during the TDS cycle. The absorption of H_2 in a D_2-loaded sample was investigated at two temperatures, and no obvious influence of the preexisting species in the rate of absorption of H_2 was seen. Moreover, deuterium absorption takes place at a higher rate than that of hydrogen and the composition of the TDS-released gas matches with that of the absorbed isotopic mixture.

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