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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.

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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}).

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.

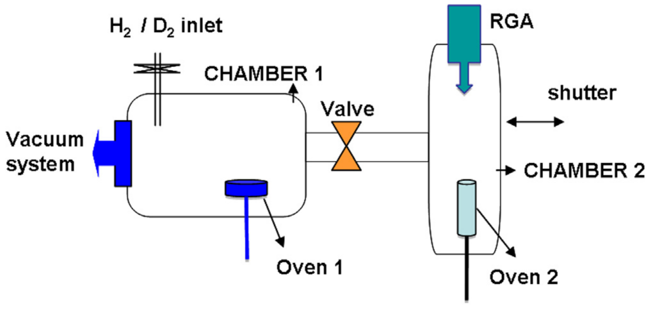

Fig. 1. Experimental set-up.

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, α 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, β 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 7.14×10^{-6} s^{-1} cm^{-2} at 473 K and 673 K, respectively).

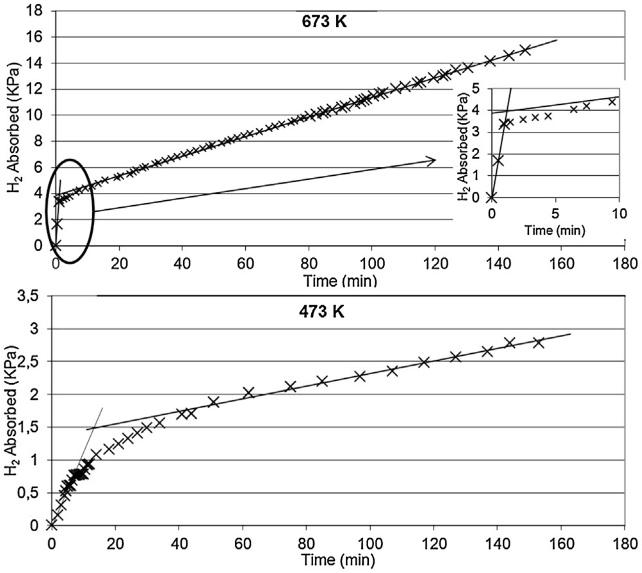

Fig. 2. Corrected H_2 pressure drop over time during the H_2 absorption experiments in lithium for the two studied temperatures, 473 K and 673 K. Solid lines represent the linear fitting to the two observed absorption phases.