Recombination of deuterium atoms on the surface of molten Li–LiD

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Abstract

Measurements of the rate constant k_r describing the surface recombination of deuterium atoms into molecules, were made for various molten mixtures of Li–LiD using a thermal desorption technique. The results are found to follow an Arrhenius relationship in the temperature range 573–873 K and are compared to the prediction of a kinetic model for the release of hydrogen from metals. The data are lower than would be predicted by the model for an atomically clean surface, but lower than predicted recombination rates are ubiquitous with this type of measurement and well known to result from surface contamination, which reduces surface-site availability and gives rise to variations in the surface chemisorption potential.

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1. Introduction

Flowing liquid–metal walls for magnetic-fusion devices promise the ability to accommodate high-incident-power density, remove heat, allow better control over tritium accumulation, and recover more easily from erosion and ablation events owing to the self-healing nature of a liquid surface [1–3]. Liquid lithium is considered an attractive candidate for this role not only because of its high-heat capacity, but also because it is low in atomic mass and has a high solubility for dissolved-lithium hydride [4,5], which further promises low rates of hydrogen recycling to the plasma: an influence generally well known for improving edge plasma temperature and core plasma performance.

Low recycling is expected because the reaction of lithium with hydrogen is strongly exothermic, resulting in bound hydrides that become trapped in solution [6–13]. However, it has long been known [6] that lithium hydride, when dissolved in molten lithium, thermally decomposes at temperatures well below the melting point of pure lithium hydride (∼960 K) under conditions of vacuum, or when the hydrogen partial pressure in contact with the melt is too low [7]. Bulk diffusion and atom recombination into molecules on the surface are two physical processes that strongly govern the rate of hydrogen desorption from metals. Yet, hydrogen diffusion in liquid lithium is extremely rapid [14,15] and not strongly activated with temperature, so the release kinetics are rate limited by recombination [16]. Knowledge of the recombination rate with temperature is therefore crucial to understanding recycling from liquid-lithium first-wall or plasma-facing components.

2. Recombination theory

Where the recombination of atoms into diatomic molecules limits transport of a dissolved solute gas

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across a metal–gas boundary, a recombination constant k_r can be defined [17] such that

$$k_r = J/c^2, \tag{1}$$

where J is the net flux of outbound gas molecules and c is the solute gas concentration immediately below the surface. Although traditionally applied to solid metal surfaces [17,18], this definition is equally applicable to a liquid metal surface provided that transport across the surface is indeed rate limited by recombination, and outgassing due to fluid effects such as bubble formation or turbulence, for instance, are negligible.

Numerous authors [17–20] have modelled the recombination rate for hydrogen isotopes on metallic surfaces and good agreement between the models exists in their application to metals that react exothermically with hydrogen. Here we have focussed on the most recent treatment provided by Pick and Sonnenberg [20]. Pick and Sonnenberg's recombination rate is given by

$$k_r = \phi s/\kappa^2, \tag{2}$$

where ϕ relates the arrival rate of gas molecules at the surface to the gas pressure, and s and κ are the temperature dependent relations for the sticking probability and the proportionality constant in Seiverts' law. Each of these quantities is given by

$$\phi = 2.63 \times 10^{24}(2MT)^{-1/2} \quad (\text{m}^{-2}\,\text{s}^{-1}\,\text{Pa}^{-1}), \tag{3a}$$

$$\kappa = \kappa_0 \exp(-E_s/kT) \quad (\text{m}^{-3}\,\text{Pa}^{-1/2}), \tag{3b}$$

$$s = \sigma \exp(-2E_c/kT), \tag{3c}$$

where M is the atomic mass in u of the desorbing species, T is the temperature in K, κ_0 is the prefactor in Seiverts' constant, E_s is the enthalpy of solution, σ is a constant related to surface-site availability, and E_c is the activation energy for chemisorption at the surface. Substitution of Eqs. (3a)–(3c) into Eq. (2) gives

$$k_r = 2.63 \times 10^{24}(\kappa_0)^{-2}\sigma(2MT)^{-1/2}\exp(2[E_s - E_c]/kT)$$
$$(\text{m}^4\,\text{s}^{-1}). \tag{4}$$

For an ideally clean surface, σ can be taken to be unity and E_c reduced to zero for metals that react exothermically with hydrogen. In this instance, the only energy barrier for hydrogen release is the intrinsic heat of solution E_s for dissolved hydrogen in the metal. In realistic scenarios though, where the influence of contaminant impurities on the surface of the metal always lowers the recombination rate, $\sigma < 1$ describes the reduction in available surface sites by occupation with impurities, and $E_c \sim 0.1$ eV [20] is the associated energy barrier that must be further overcome for the hydrogen to be released.

3. Experimental procedures and analysis

The recombination rates for surface deuterium on molten solutions of deuterium and lithium were established from simple thermal desorption analyses. In particular, and with reference to Eq. (1), the technique involved determining simultaneously the quantities J and c for various solution temperatures. The outbound D_2 flux, J, was obtained from a calibrated measurement of the D_2 partial pressure. However, determination of the surface deuterium concentration, c, responsible for producing the recombining D_2 flux, was not as straightforward. Here the concentration c was inferred from the equilibrium solubility data of Veleckis et al. [11] in the temperature range chosen for this study. Based on their observations of the unique way in which solutions of deuterium and lithium decompose under conditions of equilibrium, an accurate method for inferring c with temperature could be made here.

To elaborate, we note the equilibrium Li–LiD phase diagram of Fig. 1, which has been produced from solubility and pressure-composition-temperature (PCT) isotherm data available in the literature [7,9,11–13]. The dashed lines enclose the temperature range in which measurements of the recombination rate were made. The symbols show the compositions of the three Li–LiD solutions used in this study at the maximum temperature attained during desoption. Each sample solution was
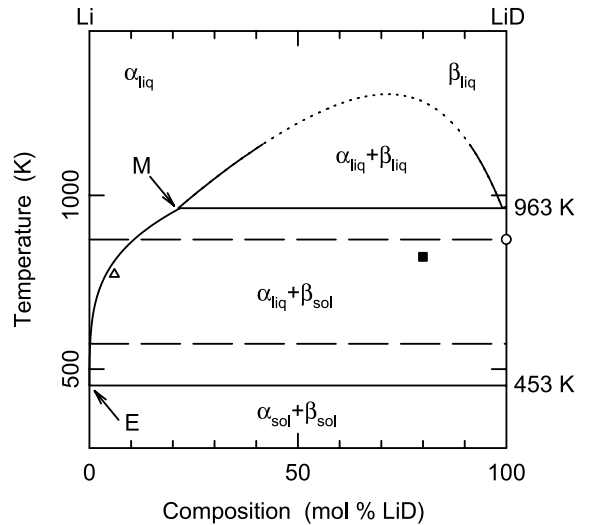

Fig. 1. Li–LiD phase diagram produced from solubility and PCT isotherm data taken from the literature [7,9,11–13]. The horizontal dashed lines define the temperature range explored for determining recombination rates. Sample compositions: D/Li of 0.1 ($\triangle$), 0.8 ($\blacksquare$) and 1.0 ($\circ$) are indicated for their maximum outgassing temperature. The dotted line shows the predicted closure of the $\alpha_{liq} + \beta_{sol}$ region but remains to verified experimentally (e.g. see Ref. [13]).

produced from a separate amount (∼0.1 g) of pure lithium (99.9%) that was exposed molten (∼620 K), to a high flux (∼1 × 10^{22} D ions $m^{-2}\,s^{-1}$. Here the D^{+}:D_2^{+}:D_3^{+} ratio was 75:5:20 at the pressure used (∼133 mPa).) deuterium plasma in the PISCES-B linear-edge-plasma simulator [21,22] for various lengths of time.

To establish the deuterium concentration c, it is important to note that the overall composition of the samples studied were in the $\alpha_{liq} + \beta_{sol}$ region during desorption analysis. That is, there was the coexistence of a liquid phase (α_{liq}) and a solid phase (β_{sol}) in the sample melt. The α_{liq} phase is a solution of dissolved deuterium in liquid lithium, fixed in deuterium solubility (defined by the liquidous curve connecting the eutectic (E) and monotectic (M) points [11–13]), while the compositional balance consists of precipitates of the β_{sol} phase (solid LiD). To reiterate, measurements of the recombination rate were made during the thermal desorption of molten Li–LiD solutions with conditions as close as possible to equilibrium. When at equilibrium, desorption of hydrogen isotopes takes place with gas phase hydrogen in contact with the melt remaining constant in pressure [7,9,11] until the sample is depleted of all β_{sol} phase. In a two step process, precipitates of β_{sol} phase dissolve back into solution to maintain the fixed solubility concentration of the α_{liq} phase, which in turn loses hydrogen to the gas phase. Determination of c is thus made by noting that the recombination flux originates only from the α_{liq} phase, which conveniently is fixed in deuterium solubility (given by the $\alpha_{liq} - (\alpha_{liq} + \beta_{sol})$ liquidous in Fig. 1). That is, precipitates of β_{sol} phase do not contribute to the recombination flux, since the α_{liq} phase is the ensuing step in the decomposition of β_{sol}. The only caveat is that the exposed surface of the melt must consist entirely of the α_{liq} phase. However, while precipitates of β_{sol} phase might be expected on the surface, kinetic models [16] describing the thermal decomposition of particulates of β_{sol} metallic hydride show that the surfaces of particulates rapidly convert to α_{liq} phase. That is, the surface ought to be uniformly liquid and of the α_{liq} phase composition.

Measurements of the recombination flux J, as a function of temperature, were separately made for each sample of molten Li–LiD using thermal desorption mass spectrometry (TDS) [23]. TDS analysis involved heating the sample in vacuo and monitoring the partial pressure of various species outgassed (e.g. D_2, HD, HDO, D_2O, LiD) from the sample with a residual gas analyser (RGA). The RGA $m/q = 4$ peak (i.e. D_2) was calibrated with a standard flow of deuterium to allow the conversion of D_2 partial pressure into molecule flux.

Measurements of the recombination rate are extremely sensitive to the nature of the surface; variations between experiments extending orders of magnitude have been found [20]. Adsorbed or chemically bound surface oxygen is known to be a strong influence in such experiments and is a widely known cause for lower than expected recombination rates in comparison with the predictions of kinetic models [20], where the assumption is made that the surface is atomically clean. With lithium, this influence is largely unavoidable, even under vacuum. Lithium reacts chemically with residual oxygen and water vapour to form Li_2O and LiOH [24] and in a previous study using X-ray photo-electron spectroscopy [25], we have found that monolayer coverage in predominately Li_2O occurs within minutes on a clean lithium surface in vacuum (∼10^{-6} Pa), when solid. However, in the course of our studies with liquid lithium we have also found that surface contamination, if not too severe, will begin to visually disappear at ∼550 K as the sample is heated. Actually, this is not all that surprising since small amounts of oxygen are quite soluble in liquid lithium [5], and interestingly, this seems to correspond to TDS desorption maxima that are observed. Fig. 2 shows this for a typical set of desorption profiles taken on a sample of molten $\alpha_{liq} + \beta_{sol}$ Li–LiD. The evolutions of masses 4 (D_2), 18 (H_2O), 20 (D_2O) and 32 (O_2) are shown. Desorption maxima (centered around ∼550 K) are observed in the profiles for H_2O, D_2O and O_2 as the temperature is increased and are consistent with the thermal decomposition of the surface hydroxides LiOH and LiOH · H_2O [26] and their corresponding deuterium isotopes. Further temperature increase to 673 K results in a fall in H_2O, D_2O and O_2 partial pressures.

In the constant temperature region of Fig. 2 the D_2 profile shows a trend that is unchanging with time and can last many hours depending on the temperature. For
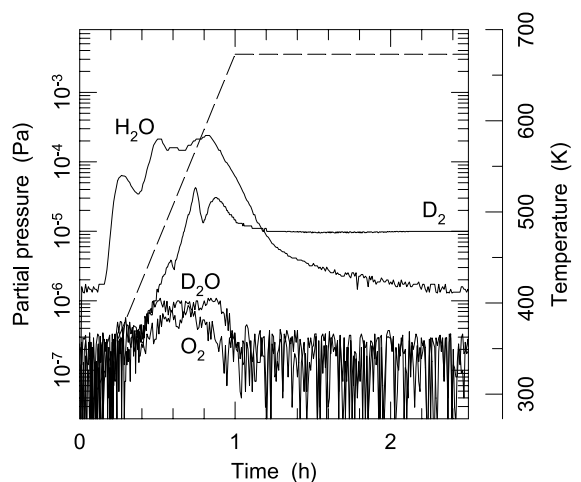

Fig. 2. Outgassing profiles for masses 4 (D_2), 18 (H_2O), 20 (D_2O) and 32 (O_2) taken on a sample of Li–LiD using the programmed temperature sequence indicated by the dashed line.

various temperatures we have explored, the D_2 partial pressure typically resembles a plateau and closely reflects the equilibrium thermal decomposition of molten Li–LiD solutions [7]. Thus, the plateau partial pressure, once measured as a function of temperature and converted to recombination flux, can be used along with the corresponding values for the equilibrium solubility of deuterium in the α_{liq} phase as a function of temperature, to find the temperature dependence of the recombination rate.

Based on this, each sample of Li–LiD solution was desorbed in the following way. The sample was elevated to 773 K to reduce surface contamination and H_2O, D_2O and O_2 peaks noted to fall before cooling to ambient temperature. Then the sample was reheated in stepped temperature increments to observe plateaus at various fixed temperatures.

4. Results

Fig. 3 shows a stepped desorption profile for the sample of Li–LiD that had a concentration of 0.8 D/Li. The ordinate in Fig. 3 has been converted to molecule flux and a trend in D_2 release reflecting the temperature profile is shown. At each fixed temperature step (A–F), the outward D_2 flux is seemingly constant except for the highest temperature plateaus (E and F) where departure from equilibrium at high temperature may be evident. At high temperature both the evolved D_2 partial pressure and the vapour pressure of Li are relatively high, leading to rapid changes in the overall solution con-

centration and large rates of Li evaporation. Surface and gas phase influences due to evaporation are unclear in the current experiment since the loss rate for Li from a Li–LiD solution is unknown. However, these influences should not be as severe at the lower temperature steps as vapour pressure falls exponentially with decreasing temperature. Other than this, additional concern lies in the formation of LiD in the gas phase, or HD due to isotope exchange with residual hydrogen at the walls; both effects that would reduce the measured D_2 molecule flux. However, we see no evidence for gaseous LiD with the RGA, and it should not accumulate on the hot walls of the TDS system because of its high decomposition pressure [9]. In the case of HD formation, the partial pressure for $m/q = 3$ was typically small compared to that for D_2, but where significant, a correction to the D_2 partial pressure was applied using the same flow calibration as for D_2.

Recombination rates, determined using Eq. (1) are plotted as a function of reciprocal temperature in Fig. 4. To facilitate this, we have used the plateau pressures (as in Fig. 3) for each of the three samples outgassed.
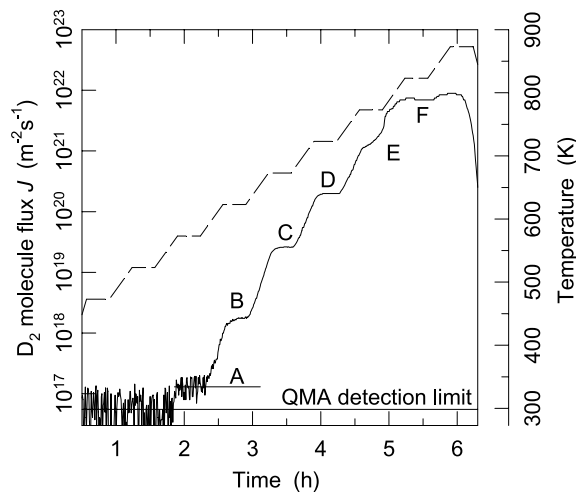

Fig. 3. Outgassed D_2 molecule flux for the sample of Li–LiD with a mole fraction of 0.8 D/Li for the stepped temperature profile indicated by the dashed line. Labels A–F depict constant temperature 'plateaus'.
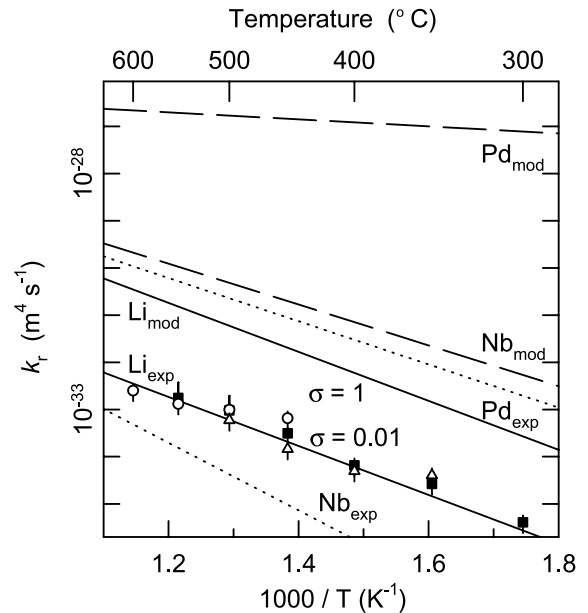

Fig. 4. Recombination rates plotted as a function of reciprocal temperature. The symbols show recombination rate data for each of three samples – D/Li composition: 0.1 ($\triangle$), 0.8 ($\blacksquare$) and 1.0 ($\bigcirc$). The solid lines are the prediction of Eq. (4): Upper line – clean surface ($\sigma = 1$), $E_s = -0.53$ eV atom^{-1} and $\kappa_0 = 3.13 \times 10^{23}$ m^{-3} Pa$^{-1/2}$. Lower line – weighted least squares fit, $\sigma = 0.01$. For comparison, experimental hydrogen recombination rates (dotted lines) are plotted for Pd and Nb [20] together with their corresponding model predictions [20] (dashed lines) by Eq. (4) for clean surfaces (i.e. $\sigma = 1$).

Equilibrium solubility values for the α_{liq} phase were taken from Veleckis et al. [11]. Each set of points reveals an Arrhenius trend with no significant influences due to the initial amount of deuteride in the sample. The lack of influence here supports the hypothesis that the recombination flux does not depend on the compositional balance of the precipitate phase. The prediction of the model, Eq. (4), for a clean Li surface ($\sigma = 1$) is also shown. Values in Eq. (4), $E_s = -0.53$ eV atom^{-1} (the average of the quoted values in Refs. [7,12,13]) and $\kappa_0 = 3.13 \times 10^{23}$ m^{-3} Pa$^{-1/2}$ [7] were taken from the literature. The line through the data is a weighted least squares fit of Eq. (4) using these same quantities and allowing for the prefactor σ in the sticking probability and the chemisorption potential E_c, to vary. Less weight was given to the points at high temperature because of suspected influences due to evaporation. Agreement with the data requires a value of $\sigma = 0.01$, and interestingly, there is no need to allow for the influence of a chemisorption potential E_c, despite having to correct for occupied surface sites by varying the quantity σ. Including the chemisorption potential reduces the quality of the fit. The need for a reduced value of σ suggests reduced surface-site availability, likely due to the presence of oxides, but the slope of the fitted line is consistent simply with the enthalpy of solution E_s for deuterium in liquid lithium, implying that $E_c \sim 0$.

Also shown are experimental hydrogen recombination rates for the metals Pd and Nb (cited in Ref. [20]), which are two other metals that also react exothermically with hydrogen. In contrast to the corresponding predictions by Eq. (4) [20] for these metals, the experimental data for Pd and Nb are even more difficult to reconcile with the model. The experimental results are low by more than several orders of magnitude. The experimental data for liquid Li therefore not only show the applicability of the model to a liquid, but in addition, accounting for surface contamination, leads to good agreement between the model and the experiment.

5. Discussion

From the data of Figs. 2–4, it is clear that liquid lithium loses hydrogen to surrounding vacuum by a recombination-limited gas release mechanism. In a reactor relevant scenario, the operating temperature for liquid lithium needs to be kept below 650 K [27] to prevent significant evaporative Li influx to the edge plasma. For lithium with a hydrogen inventory of at least the α_{liq} phase composition, hydrogen loss rates from solution are extremely low below this temperature, as revealed by the stepped D_2 flux profile of Fig. 3. Here, the outward D_2 flux is less than 10^{20} m^{-2} s^{-1} and falls exponentially as the operational temperature is reduced. Furthermore, the loss rate is independent of the amount of any pre-

cipitated hydride that may be present, albeit that operating the lithium in a highly saturated mode where hydride precipitates have formed would be unlikely in a reactor scenario because of safety concerns over accumulated tritium. Nevertheless, this loss rate, defined by the solubility limit for hydrogen isotopes in liquid lithium, represents a static upper limit. For concentrations of dissolved hydrogen isotopes below the solubility limit, the recombination flux is lower since it varies with the square of the concentration. Based on this, extremely low rates of recycling seem possible. As an example, for an incident ion flux of $\sim 10^{23}$ m^{-2} s^{-1} such as in the diverter of a tokamak, an outward hydrogen flux of 10^{20} m^{-2} s^{-1} would imply only 0.1% recycling on taking a simple particle balance approach. However, here other effects such as material erosion for example [22,28], would have to be negligible.

The recombination data shown in Fig. 4 reflect the strong hydrogen trapping capability of exothermic absorbers of hydrogen, and, as implied by the model [19,20], the data show only a strong dependency on temperature, when ignoring surface-impurity effects. To our knowledge, no other measurements of the recombination rate for hydrogen on a liquid-lithium surface have been made. However, it is worth mentioning that Liao et al. [29] estimated the recombination rate for hydrogen on liquid lithium through analysis of the ion-burial experiments of Erents et al. [30], where it was found that near unity trapping efficiency exists for 18 keV D$^+$ ions incident on a pool of liquid lithium. Liao et al. estimated the recombination rate as $k_r = 2.3 \times 10^{23} D$ m^4 s^{-1}, where D is the diffusivity of hydrogen in liquid lithium. The dependence on D however, prevents a thorough comparison with our data because of the orders of magnitude variations between reported diffusivities in the literature [14,15,31].

6. Conclusions

In the temperature range 573–873 K, the atomic to molecular surface recombination rate for deuterium on molten Li–LiD, is found to follow an Arrhenius trend with a slope consistent with the enthalpy of solution for deuterium in liquid lithium. The results, when compared with the prediction of the hydrogen release model of Pick and Sonnenberg [20], are lower than for an atomically clean surface. However, lower than predicted recombination rates, are ubiquitous with this type of measurement and well known to result from surface contamination, which reduces surface-site availability and gives rise to variation in the surface chemisorption potential. In addition, the experimental data reveal an applicability of the model to liquid metals, and when accounting for surface contamination, good agreement between model and experiment is found.

Acknowledgements

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