A Study on Hydrogen Transport in Liquid Metals under Steady State Plasma Bombardment

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Hydrogen Plasma-driven Permeation (PDP) experiments through two different liquid metal membranes: lithium and GaInSn have been conducted in the temperature range from 300 to 500 °C. A technique employing a mesh sheet to hold a liquid metal for PDP has been utilized for the first time. It has been found that PDP is surface recombination limited for lithium and is diffusion limited for GaInSn. Hydrogen surface recombination coefficients for liquid lithium and hydrogen diffusivity in GaInSn have been obtained respectively.

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1. Introduction

The application of liquid metals as plasma facing materials (PFM) draws increasing interest as a potential means to resolve the technical issues associated with exhaust power and particle handing in magnetic fusion devices [1, 2]. Molten lithium is one of the candidates for this application because of its low atomic number and high absorptivity of impinging species. It has been used in fusion devices including NSTX [3] and EAST [4]. In these confinement devices, it is considered that the interaction of hydrogen plasma with liquid lithium plays an important role in determining edge plasma characteristics and hence core confinement performance.

GaInSn is a kind of liquid metal at room temperature, and has been used for modeling of various liquid metal processes in industrial field and MHD study for flowing liquid metal owing to the low reactivity and toxicity of its components [5, 6]. In J×B-force convected liquid metal experiment, flowing GaInSn has also shown ability of reducing both hydrogen and helium recycling when facing to plasma bombardment [7]. Then it is deduced that GaInSn is also promising as a PFM in fusion reactors, though more information is needed to evaluate the feasibility.

Fick's laws have been successfully applied to describe hydrogen diffusion in solid materials in the field of plasma-wall interaction [8, 9]. Hydrogen diffusivities in the bulk of materials and hydrogen recombination coefficients at the surface of materials are essential parameters to study hydrogen retention in materials and hydrogen transport, including hydrogen permeation and hydrogen recycling. However, hydrogen diffusivities in liquid lithium show several orders difference in literature, and opposite opinions are existed about that if the surface reaction rate is a dominant process for hydrogen transport in liquid lithium [10, 11]. For GaInSn, no information related to hydrogen transport is available in literature as we know. Due to their critical importance to the application of liquid metals in fusion reactors, these technical issues must be clearly addressed.

In the present work, experiments on hydrogen PDP though liquid lithium and GaInSn membranes have been conducted, holding liquid metals on a sheet mesh by surface tension. PDP through solid titanium membranes have also been conducted as a step prior to liquid lithium in this work, due to titanium and liquid lithium are both hydride forming metals. Hydrogen permeation breakthrough curves have been obtained experimentally, as well as temperature effects on steady state PDP flux.

2. Experimental
2.1 VEHICLE-1 facility

Shown in Fig. 1 is the PDP setup for liquid metals in a laboratory-scale linear plasma device, VEHICLE-1. Details of VEHICLE-1 facility and its plasma diagnostics have been described elsewhere [12]. In this work the electron temperature is ~ 10 eV and the plasma density is of the order of 10^{10} cm^{-3}. The ion bombardment flux is of the order of 10^{16} H/cm^{2}s, and the bombarding energy is set at 100 eV by applying a negative DC bias on the sample tray. A liquid metal sample is fixed in such a way that the upstream surface is exposed to hydrogen plasma, while the downstream side is pumped to ultrahigh vacuum (10^{-6} - 10^{-5} Pa). And the two chambers are sealed by the liquid metal. The plasma-facing area is 6.6 cm^2, and the total area of openings is 0.66 cm^2. The thickness of lithium
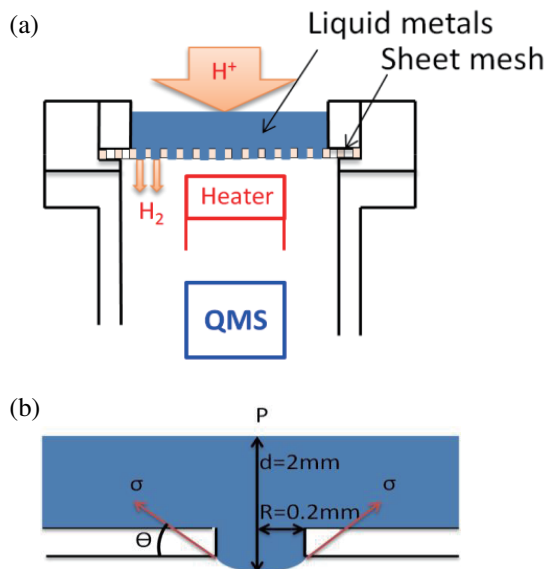
(a)

(b)

Fig. 1   (a) Schematic diagram of the experimental setup for PDP through liquid metals. (b) Surface tension to hold a liquid metal.

Fig. 2   Temperature dependence on the hydrogen steady state PDP flux through titanium membranes with thickness of 0.1 mm and 1 mm.

is ~ 2 mm before melting, and the thickness of GaInSn is ~ 6 mm. A resistive heater is positioned beneath the mesh to control the sample temperature, which is measured by a thermocouple. The hydrogen permeation flux due to PDP is monitored by the partial pressure of H_2 measured by a quadrupole mass spectrometer (QMS).

2.2   The mesh-surface tension method

The use of a sheet mesh to hold a liquid metal sample is based on the assumption that surface tensions of liquid metals are relatively high [13, 14]. To avoid liquid metal dropping down through the mesh, upward force provided by the surface tension should be larger than the weight of liquid metal and pressure difference caused by gases in upstream chamber. Shown in Fig. 1 (b) is the stress balance on liquid lithium set on the mesh, which can be described by:

$$\sin\theta \times 2\pi R\sigma = \pi R^2 \left(P + \rho g d\right), \quad 0° < \theta \le 90°. \quad (1)$$

Where σ is the surface tension of liquid lithium, R is the radius the pore, d is the thickness, ρ is the density, and P is neutral gas pressure in upstream chamber, θ is the angle between the direction of surface tension and horizontal line. In our experiments, the radius of the pores R is 0.2 mm, and typical hydrogen pressure P in upstream chamber for running plasma is ~ 0.1 Pa. For liquid lithium with thickness of 2 mm at 500 °C, surface tension σ is 0.356 N/m. Then θ will be 0.17° calculated from equation (1), which suggests that surface tension is sufficient to hold liquid lithium.

3.   Results and Discussion

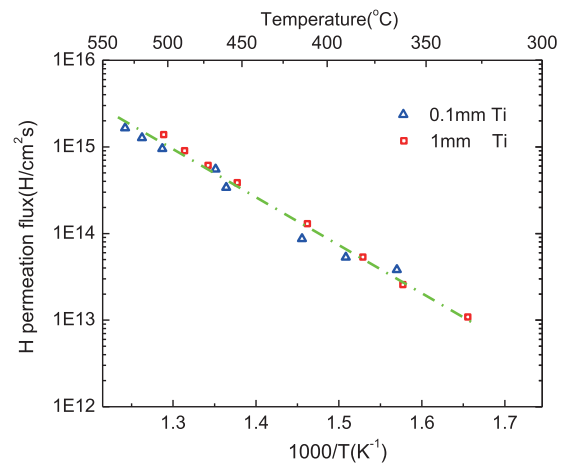In the steady-state PDP model, three regimes are considered [8]: (1) the DD-regime: diffusion limited release of hydrogen from both the upstream and downstream surfaces; (2) the RD-regime: recombination limited release from the upstream surface and diffusion limited release from the downstream surface; (3) the RR-regime: recombination limited release from both surfaces. The steady state PDP flux is inversely proportional to the membrane thickness for the DD-regime and the RD-regime, while it is independent of the membrane thickness for RR-regime.

3.1   Titanium

Hydrogen steady state PDP fluxes through 0.1 mm and 1 mm titanium membranes have been obtained in the temperature range from 331 to 532 °C. As shown in Fig. 2, there is no thickness effect on the steady state PDP flux. Then, it is concluded that PDP through titanium under these conditions is surface recombination limited.

In this experimental temperature range, the hydrogen steady state PDP flux is in the range from 1.09×10^{13} H/cm^{2}s to 1.65×10^{15} H/cm^{2}s, and the surface recombination coefficient derived from [15] is in the range from 1.2×10^{-28} cm^4/s to 3.7×10^{-27} cm^4/s. Then, the hydrogen concentration in titanium at steady state is evaluated to be in the range from 3.01×10^{20} H/cm^3 to 6.68×10^{20} H/cm^3, which shows high dynamic retention of hydrogen in titanium during PDP.

3.2   Lithium

Hydrogen PDP experiments on liquid lithium have been conducted in the temperature range from 313 to 402 °C. The Pressure-Concentration-Temperature (PCT) diagram of the LiH-Li system has been obtained based on the data evaluated by H. Borgstedt [16], as shown in Fig. 3.

The equilibrium pressure of LiH-Li in the temperature range from 313 to 402 °C is from 4.5×10^{-4} Pa to 9.1×10^{-2} Pa. And the corresponding hydrogen solubility limit is from 1.76×10^{20} H/cm^3 to 5.82×10^{20} H/cm^3, taken from the PCT diagram. The pressure in the upstream
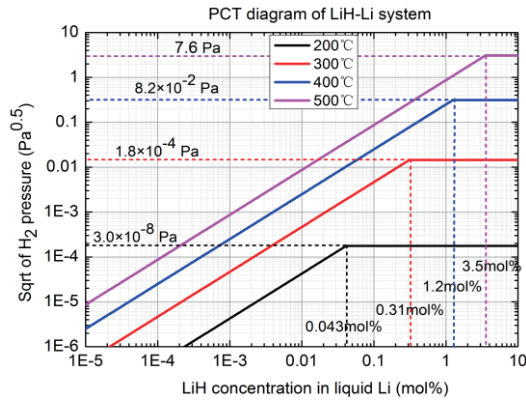
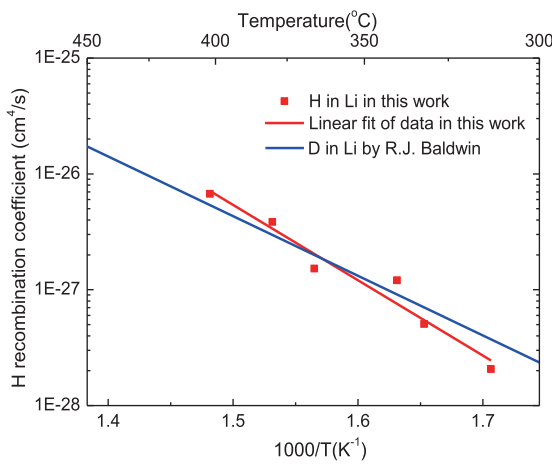Fig. 3 Pressure-Concentration-Temperature (PCT) diagram of the LiH-Li system.

Fig. 5 Comparison of experimental data and simulation results on hydrogen PDP breakthrough curve for liquid lithium.

Fig. 4 Hydrogen recombination coefficients for liquid lithium.

Fig. 6 Comparison of Hydrogen diffusivities in liquid lithium.

chamber (0.1 Pa) for running plasma is higher than the equilibrium pressure of LiH-Li, so there is no reemission flux at the upstream surface of lithium. And the measured hydrogen permeation flux at steady state is in the range from 6.36×10^{12} H/cm^{2}s to 2.12×10^{15} H/cm^{2}s, which is less than the implantation flux at upstream. Therefore the dissolved hydrogen concentration in lithium will always increase until solid LiH starts to precipitate at the upstream surface, meaning the LiH-Li system will transform from α_{liq} phase to $\alpha_{\text{liq}}+\beta_{\text{sol}}$ phase. Then dissolved hydrogen concentration at upstream surface is fixed to be the hydrogen solubility limit.

In the experiment, the steady state permeation flux is established within 3 hours, which shows a big difference compared with time lag t_{lag} based on the assumption of diffusion-limited PDP. So hydrogen PDP through liquid lithium is not diffusion limited but recombination limited, which has been found in titanium as well.

For recombination limited PDP, the hydrogen concentration at downstream surface is approximate to the dissolved hydrogen concentration at upstream surface when the steady state permeation flux is established. Then the recombination coefficient K_r can be obtained by equation:
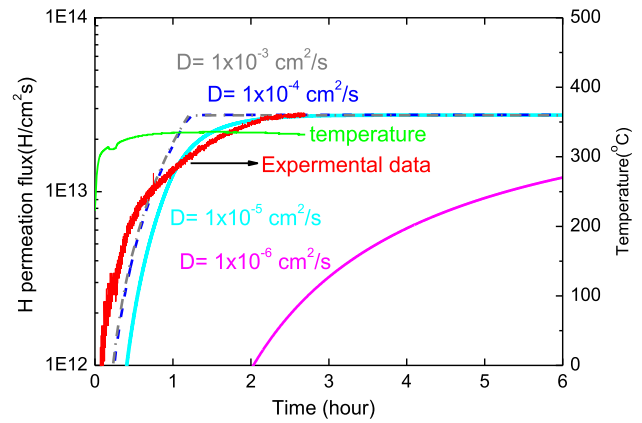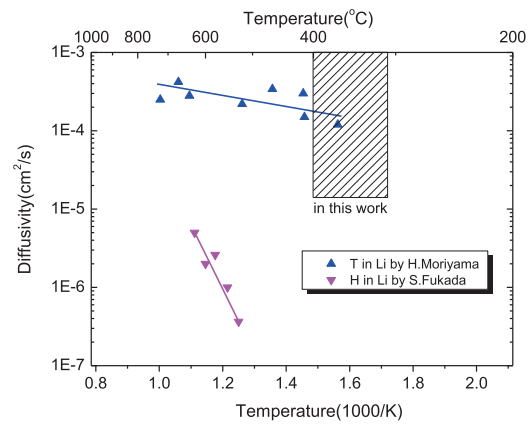
$$K_r = \frac{J^2}{C_s}. \tag{2}$$

Where J is the steady state PDP flux and C_s is the dissolved hydrogen concentration at downstream surface. The temperature dependence on hydrogen recombination coefficients has been obtained, which is close to deuterium recombination coefficients in liquid lithium [17], as shown in Fig. 4.

The simulation results of breakthrough curve with different diffusivity values in Fig. 5 show that diffusivities in the orders of 10^{-5} - 10^{-3} cm^2/s are all close to the experimental data. As diffusivity plays a minor role in a recombination limited PDP, to get precise diffusivities from PDP is infeasible. However, the recombination limited PDP in this work suggests that diffusivity of hydrogen in liquid lithium is sufficiently rapid, which supports Moriyama's results, as shown in Fig. 6.

3.3 GaInSn

Hydrogen PDP experiments through GaInSn have been conducted in the temperature range of from 400 to 500 °C. The temperature dependence on the steady state PDP flux is shown in Fig. 7. Hydrogen permeation break-
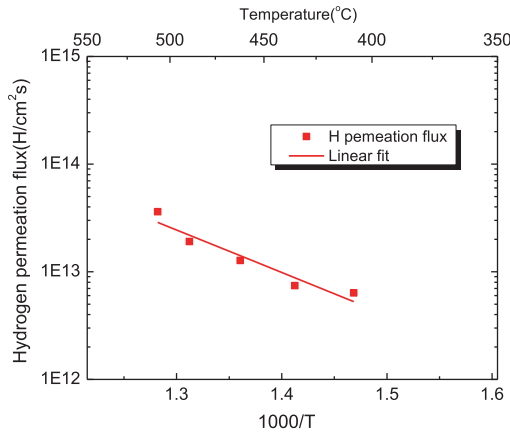
Fig. 7 Temperature effects on hydrogen PDP steady state flux through GaInSn with thickness of 6 mm.
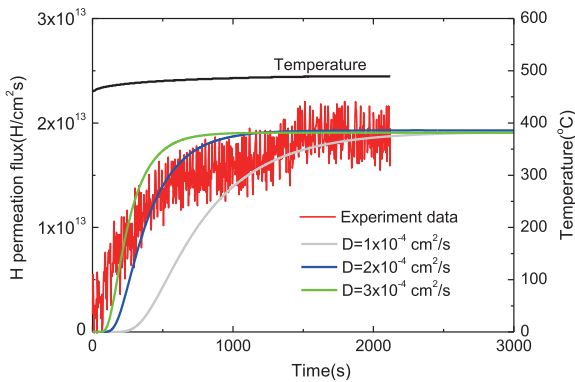

Fig. 8 Comparison of experimental data and simulation results on hydrogen PDP breakthrough curve for GaInSn.

through curve at 489 °C is shown in Fig. 8. At steady state, following equations are satisfied.

$$J = K_2 \times C_2^2, \qquad (3)$$

$$J = D \times \frac{C_1 - C_2}{d}, \qquad (4)$$

$$J_1 = J_0 - J = K_1 \times C_1^2. \qquad (5)$$

Where J is the permeation flux, J_0 is the implantation flux, J_1 is the reemission flux, d is the thickness of the sample, C_1 and C_2 is the hydrogen concentration at upstream surface and downstream surface respectively. As the diffusivity D and recombination coefficient at upstream surface K_1 and downstream surface K_2 are all unknown, K_1 = K_2 is assumed for simulation in this work. Diffusivity is set as 1×10^{-4}, 2×10^{-4}, 3×10^{-4} cm^2/s as three cases, and the corresponding recombination coefficients is 3.3×10^{-19}, 1.3×10^{-18}, 3.0×10^{-18} cm^4/s. Hydrogen permeation breakthrough curves in the three cases are compared with experimental data in Fig. 8. At 489 °C, the hydrogen diffusivity is likely to be in the range of 1 - 3 $\times 10^{-4}$ cm^2/s. And time evolution of hydrogen concentration profiles are shown in Fig. 9. It is found that hydrogen dynamic retention in GaInSn during PDP is about 4 orders magnitude lower than in titanium and liquid lithium.
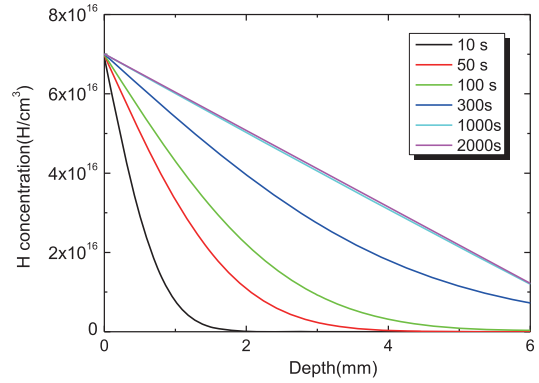

Fig. 9 Time evolution of hydrogen concentration profile in GaInSn during PDP for $D = 2 \times 10^{-4}$ cm^2/s.

4. Summary

Hydrogen PDP through liquid lithium and GaInSn has been investigated experimentally using a plasma-wall interactions facility: VEHICLE-1. A technique employing a mesh sheet to hold a liquid metal for PDP has been utilized for the first time. It has been found that PDP through titanium and liquid lithium are both surface recombination limited and is diffusion limited for GaInSn. Temperature effects on hydrogen recombination coefficients for liquid lithium have been obtained. And hydrogen diffusivity in GaInSn is found to be in the range of 1 - 3 $\times 10^{-4}$ cm^2/s at 489 °C.

Acknowledgments

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