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Gaseous hydrogen permeation through CMSII coated & ITER-grade bulk tungsten

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Abstract

Tungsten has been identified as a crucial plasma-facing material in future fusion reactors. It is considered particularly suitable for plasma facing high heat flux materials due to its high melting point, high thermal conductivity, low vapor pressure, very high threshold for sputtering, and presumably low tritium retention property. The only large-area application of tungsten to existing fusion reactors has been done in ASDEX Upgrade and is currently in progress in JET ("ITER-like wall"). Combined Magnetron Sputtering and Ion Implantation (CMSII) technology was used for W coating of carbon based materials (Carbon Fibre Composite - CFC and fine grain graphite) since only this coating method provided no deterioration during demanding thermo-mechanical tests [1]. The coating thickness was 10-15 μm or 20-25 μm depending on the position of the tile at the wall. While the thermo-mechanical and structural properties of such coating are well known, not much is known about its hydrogen interaction. The later is particularly important for the assessment of tritium retention. Due to the low hydrogen diffusivity and very small volume of W in the coated layer, the gaseous hydrogen permeation measurement at $400°C$ was selected for the experimental technique, where increasing & decreasing transient and steady state permeation flux was monitored. Problems that could arise with the CFC membrane sealing were overcome by deposition of the identical W layer on the 0.5 mm Eurofer substrate. Two such double-layer membranes were investigated. Obtained hydrogen permeability in tungsten layer ($\sim 10^{-13}$ mol H_2/m s $Pa^{0.5}$) is comparable to the upper range of published data. Measured diffusivity ($\sim 10^{-14}$ m²/s) is several orders of magnitude lower compared to the average of published data for tungsten, while the measured solubility (~ 1 mol H_2/m³ $Pa^{0.5}$) is several orders of magnitude higher. The explanation can be given in terms of hydrogen trapping that has significant impact on hydrogen migration. The membrane made from bulk ITER-grade tungsten was also investigated in our experimental setup since a considerable degree of scatter in hydrogen transport parameters is present in published data. The results obtained on CMSII coated and ITER-grade bulk tungsten are compared and discussed.

Introduction & motivation

Tungsten has been so far applied in the following fusion devices FTU and TEXTOR (limiter), Alcator C-Mod and ASDEX Upgrade (divertor) and is applied in JET "ITER-like wall" project, while planned for ITER and DEMO. In the current study we investigated the hydrogen interaction with CMSII coated W on Eurofer substrate and with bulk ITER-grade W using gaseous hydrogen permeation at 400°C. Tritium retention in the first wall and its permeation through it are namely of particular concern.

Experimental (setup, samples, measurements)

The setup for ultra-sensitive permeation measurements consisted of three separately pumped UHV chambers. Low background outgassing was achieved in the whole system. The base pressure in the analytical chamber with the MS is $\sim 3 \cdot 10^{-11}$ mbar. High sensitivity was achieved by a special thin-walled permeation cell design [2], small accumulation vol., stable T and reasonable long accumulation with F.S. 0.05 mbar capacitance gauge. The permeation flux is measured by the gas accumulation method [pressure rise method] hence $j \propto \mathrm{d}p/\mathrm{d}t$. An investigated membrane was sealed in the permeation cell by two Au 0.6 mm thick O-rings. The resulting hydrogen exposed area was 8.4 cm².
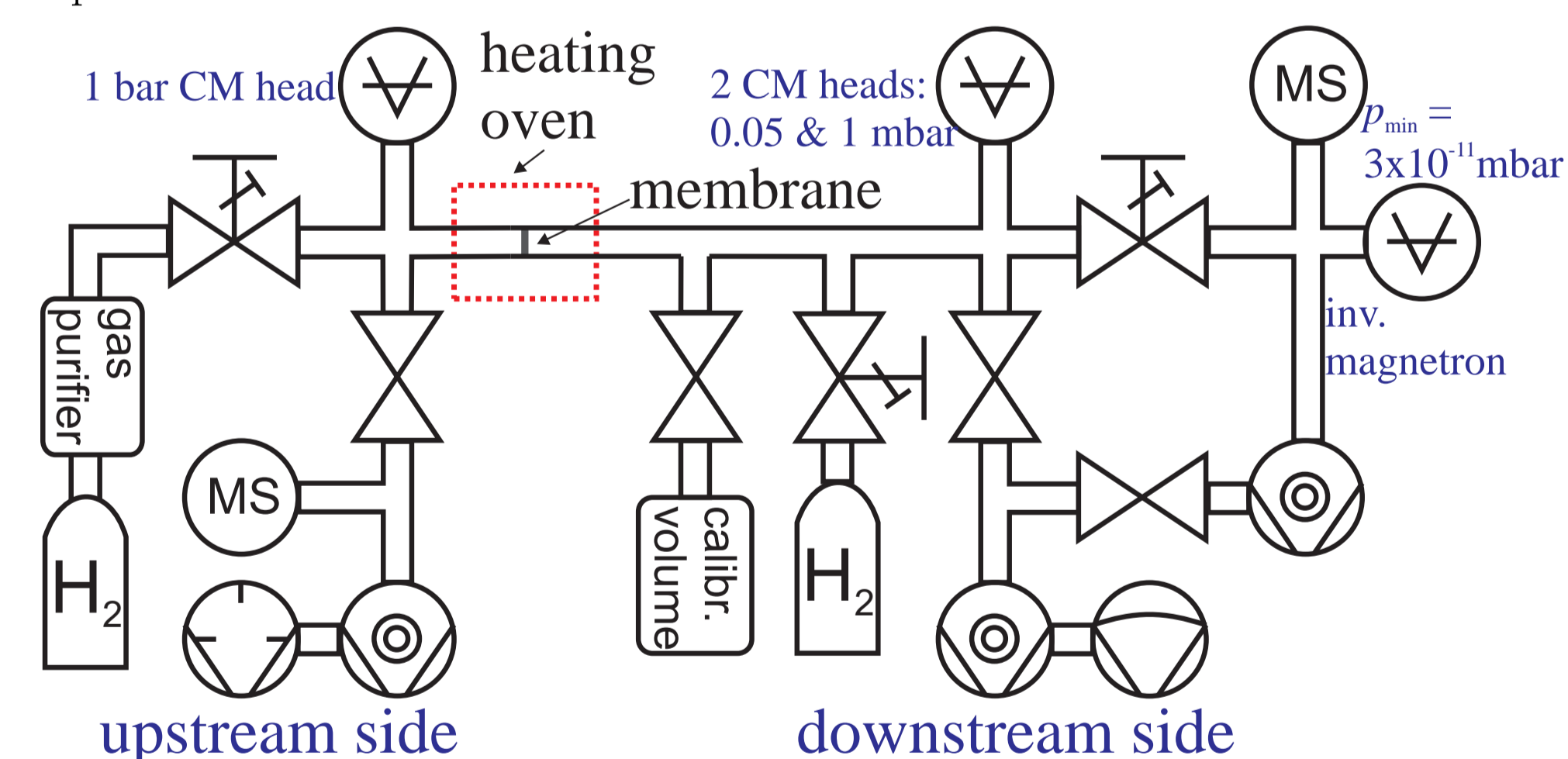
All-metal UHV system for hydrogen permeation meas. with inert gauges.

Sample preparation:

- The 10 μm W layer was coated at NILPRP by Combined Magnetron Sputtering and Ion Implantation (CMSII) technique [1]. This technique involves simultaneous magnetron sputtering and high energy ion bombardment. In the deposition process, three low pressure electrical discharges (magnetron discharge, DC bias discharge and high voltage pulse discharge) are superposed. The substrates were fine polished 0.5 mm thick, $\phi = 40$ mm disks made of Eurofer 97 (reduced-activation tempered martensitic steel). An extremely dense and pore-free nano-structure is produced by CMSII technique. At the same time, a stress relief occurs within the layer. The deposition temperature is approximately 400°C.

- Bulk tungsten (ITER-grade) was provided by Plansee AG. Production route consists of four steps: cold isostatic pressing followed by sintering $(2000 - 2500°C)$, forging in radial direction to obtain a rod with $\phi = 80$ mm, forging along the cylinder axis, removal of residual stresses by a treatment at 1000°C [3]. Material shows anisotropic microstructure. Only membranes with grains elongated in the radial direction had sufficient mechanical stability to conduct the permeation measurements. Tungsten rod was cut by electric discharge machining into the disk shaped membrane 0.5 mm thick & $\phi = 40$ mm. Then it was ground, mechanically polished to obtain an optically flat surface and cleaned.

Permeation measurements
He leak test was performed on cold and hot (400°C) membrane. After achieving sufficiently low background outgassing level (predominantly from the membrane), pure hydrogen was introduced abruptly into the upstream chamber and the upstream pressure p was kept constant at selected value in the range 0.2 - 1.2 bar. The pressure p_d at the downstream side was monitored and when it approached 3.0 Pa the accumulated gas was rapidly pumped away and the accumulation continued.

Theory

In the diffusion-limited regime the permeation flux is $j = P\sqrt{p}/d$, where p is upstream pressure, d membrane thickness and P the membrane permeability. For single layer membrane $P = DS$ holds, where D and S are hydrogen diffusivity and solubility. For two-layer membrane the effective P can be introduced as

$$\frac{d}{P} = \frac{d_1}{P_1} + \frac{d_2}{P_2} \qquad (1)$$

where indices denote layer 1 and 2, while the membrane thickness $d = d_1 + d_2$. In steady state, the permeation flux is equal through both layers, hence

$$j = D_1 \frac{C_{1,i}}{d_1} = D_2 \frac{C_{2,g} - C_{2,i}}{d_2}, \qquad (2)$$

where C denotes hydrogen concentration in the layer while indices i and g stand for concentration at the layers interface and gas facing surface, respectively. In this case the layer 2 is in direct contact with the permeation driving gas. It can be shown that the concentration ratio at the layers interface is $C_{1,i}/C_{2,i} = S_1/S_2$. Solubility and diffusivity can be extracted only from the transient permeation. The time-lag defined by the integrated-flux asymptote intersection with time axis equals $L_1 = d^2/6D$ for a single layer membrane. An expression for the time-lag for two layer membrane L_2 is also available [4]. When L_2 is converted to the effective diffusivity as $D = (d_1 + d_2)^2/6L_2$, the diffusivity of the investigated layer can be obtained from [4, 5]

$$\frac{D_1}{D_2} = (1 + 3\psi\lambda) \left((1 + \psi\lambda)(1 + \lambda)^2 \frac{D_2}{D} - \lambda^2(3 + \psi\lambda) \right)^{-1} \qquad (3)$$

where $\lambda = d_2/d_1$ and $\psi = P_1/P_2$.

Solubility of the membrane is usually obtained from $S = P/D$ relation. In the case of single-layer membrane it is possibly to directly measure the amount of hydrogen dissolved in the membrane during the steady-state permeation (linear conc. profile). It can be shown [6] that after an abrupt removal of feed gas (i.e $p \to 0$) one third of hydrogen from the membrane will outgass at the downstream side.

CMSII coated W layer on Eurofer

Our D_E, S_E and P_E coefficients for uncoated **E**urofer membranes are in very good agreement with the published data. Two nominally identical W/Eurofer membranes were investigated.
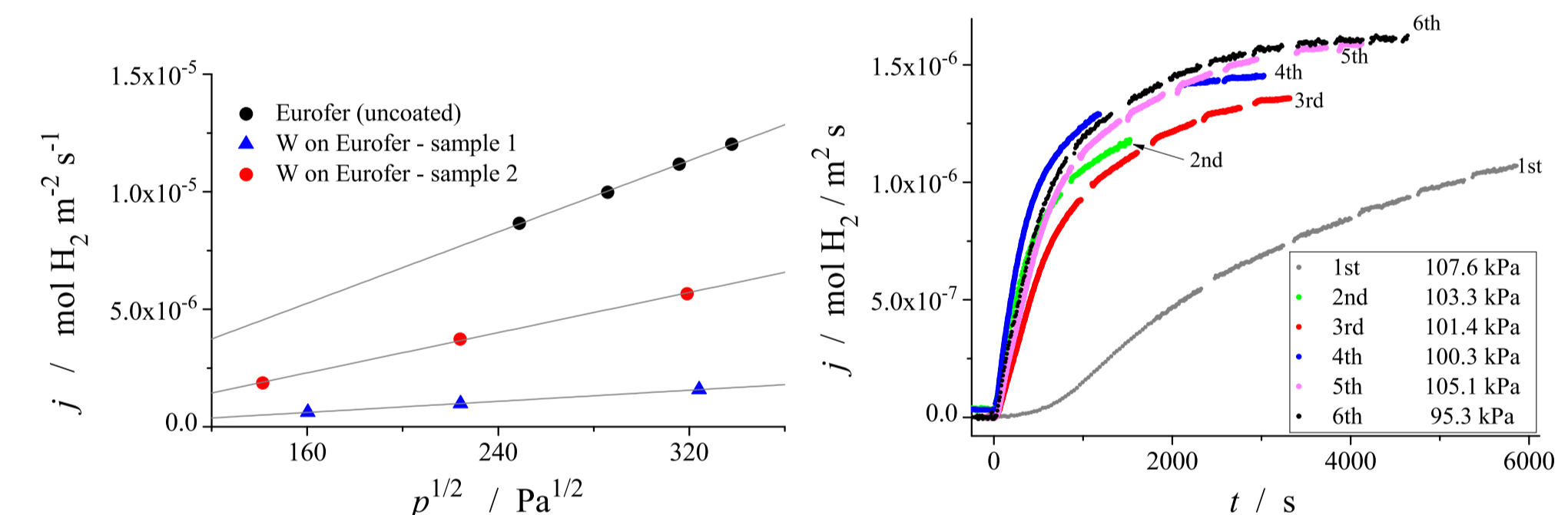
j vs p dependence ⇑ .   Initial six permeation transients (sample 1)⇑.
Permeation through bare Eurofer and W/Eurofer membranes was confirmed to be diffusion-limited as $j \propto \sqrt{p}$. From eq. (1) follows $P_{W,1} = 7.0 \cdot 10^{-14}$ and $P_{W,2} = 4.9 \cdot 10^{-13}$ mol H_2/m s $Pa^{0.5}$. A more extensive study of the hydrogen permeation kinetics was performed on the sample 1 where six permeation transients were monitored within the period of one week and the membrane was kept at 400°C. Time-lag of 800 s was measured from the sixth permeation curve, hence effective diff. is $D = 5.4 \cdot 10^{-11}$ m²/s. Cracks and pinholes do not contribute to the permeation flux as there is no rapid increase in $j(t)$ [7]. From eq. (3) follows $D_W = 2.8 \cdot 10^{-14}$ m²/s and from $S_W = P_W/D_W = 2.5$ mol H_2/m³ $Pa^{0.5}$. Both values deviate for orders of magnitude from the range of published values (D_W very low, S_W very large). We provide the following experimental evidences that support the obtained D_W and S_W:

- Inserting the known 6th curve steady-state $j = 1.62 \cdot 10^{-6}$ mol H_2/m²s in eq. (2) the $C_{E,i} = 0.127$ mol H_2/m³ can be obtained and hence $C_{W,i} = 121$ mol H_2/m³ follows from known S_W/S_E. According to Sievert's law is $C_{W,g} = 773$ mol H_2/m³. Inserting obtained concentrations into eq. (2), the right-most term deviates only 12% from the measured j value.

- A decreasing transient of permeation through W coated Eurofer membrane has been recorded after the sixth permeation curve achieved the steady state. The pressure increased for $\Delta p_d = 2.37$ Pa in 60 minutes and would have increased somewhat more if the observation period had been prolonged. Observed Δp_d corresponds to the evolution of M_{obs}. $= 5.1 \cdot 10^{-4}$ from W layer, while the expected value is $M_{\text{exp.}} = \frac{1}{3} d_W (C_{W,g} + C_{W,i})/2 = 1.5 \cdot 10^{-3}$ mol H_2/m². From M_{obs} follows a more reliable $S_W = 0.85$ mol H_2/m³ $Pa^{0.5}$. Uncoated membrane yields $\Delta p_d = 0.4$ Pa which is in good agreement with D_E and S_E. The most probable explanation for high solubility and low diffusivity in W layer is the presence of traps for hydrogen. It is well known fact that trapping enhances the hydrogen solubility and decreases the diffusivity, while it does not impact the permeability. Using Oriani's model and "average" data for bulk tungsten we obtain trap concentration $n_T = 670$ mol/m³ $\approx 6 \cdot 10^{-3}$ trap/W and their occupancy $\theta \approx 0.8$ [6].
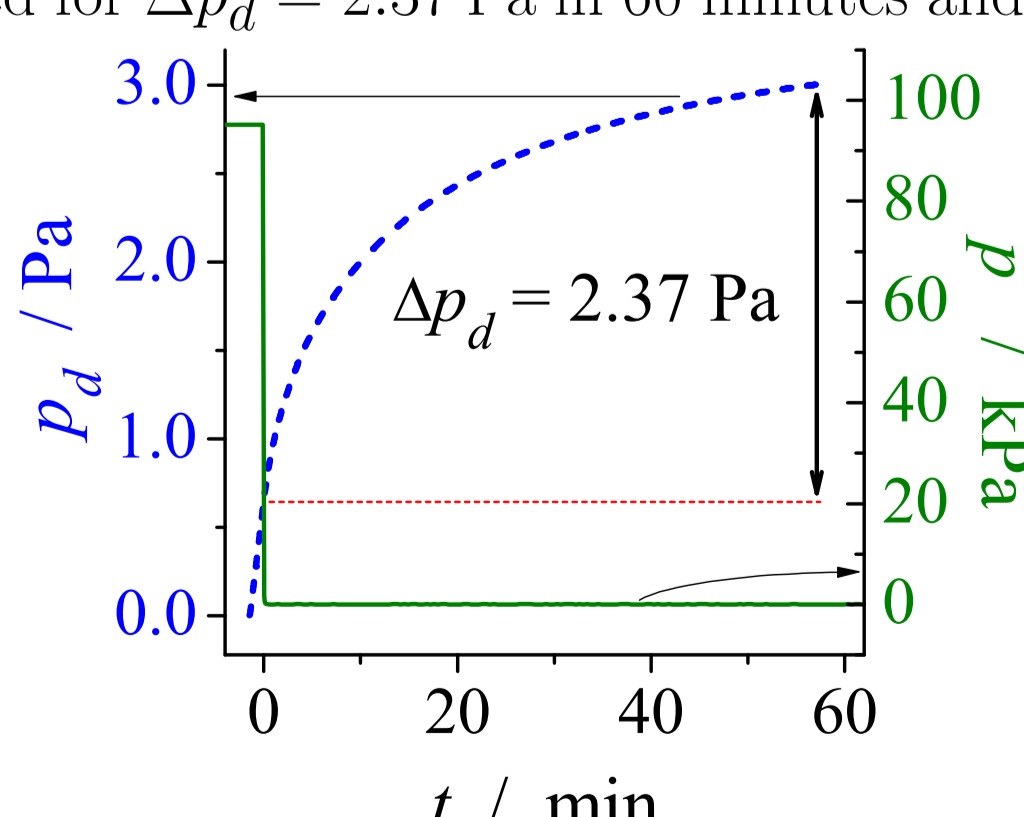

Bulk ITER-grade tungsten membrane

Large amounts of H_2 and less CO have outgassed from this membrane, while kept at 400°C for more than 10 days. Background signal was too high to observe any hydrogen permeation flux and consequently for several ten hours it was also outgassed at 450 and 500°C. The extracted hydrogen concentration amounts to several mol H_2/m³. Only after this intensive treatment the contribution of the membrane to the background outgassing was sufficiently low that we managed to observe the increase in the dp/dt once the H_2 was introduced.
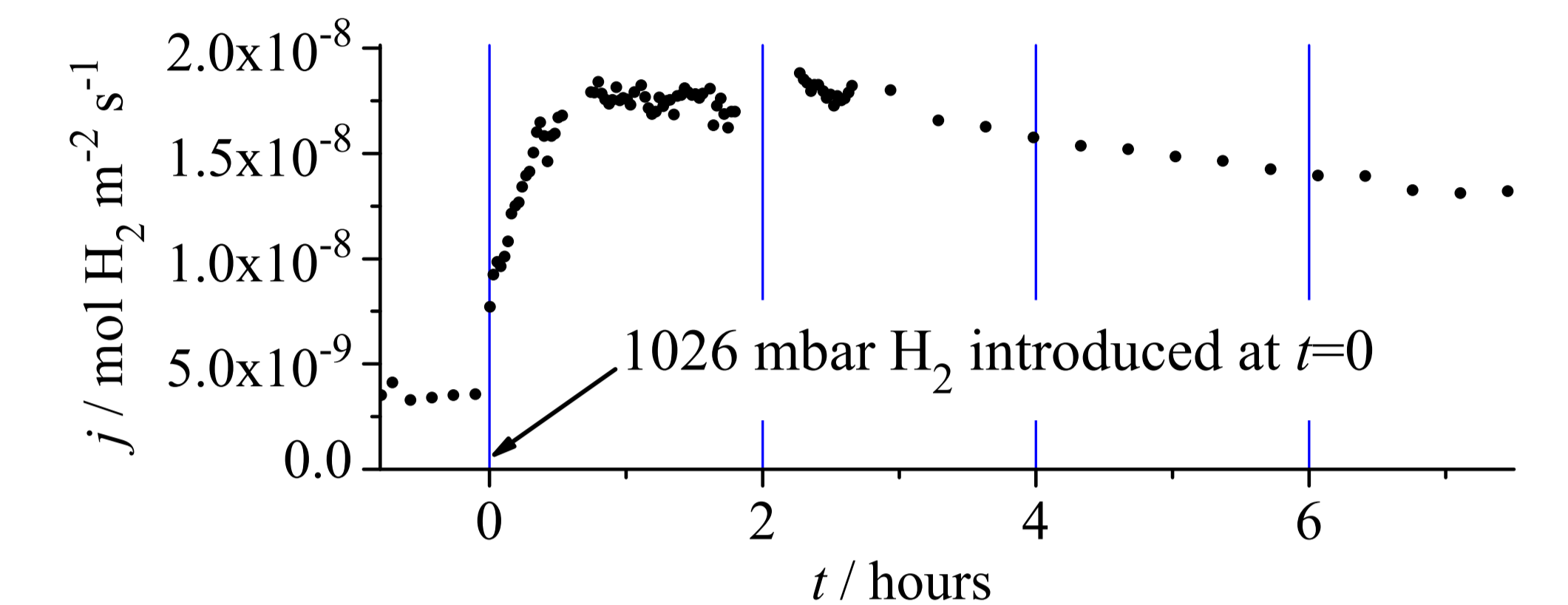
First permeation onset at 400°C. Permeability coefficient was determined to be $P_W = (0.46 - 2.1) \cdot 10^{-14}$ mol H_2/m s $Pa^{0.5}$. Almost immediate increase in the permeation flux j after $t = 0$ might suggest grain boundary diffusion. The slow decrease in j could result from the membrane inlet surface contamination.

Our and published data on W at 400°C
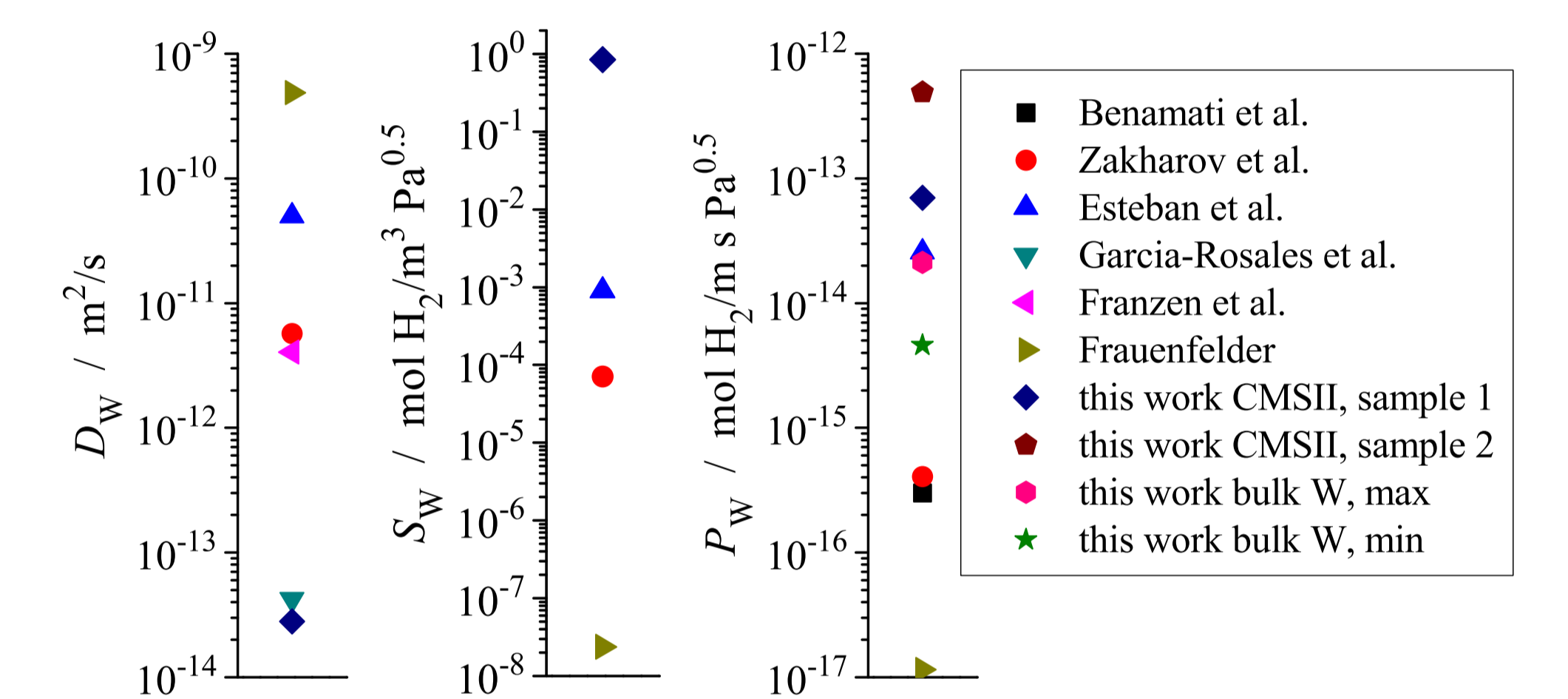
Comparison of hydrogen diffusive transport parameters obtained in our study and those published [8, 9, 10, 11, 12] that were actually measured at 400°C. Only values obtained by Frauenfelder [13] were extrapolated from high T range.

Acknowledgements

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