



# Analysis of low pressure hydrogen separation from fusion exhaust gases by the means of superpermeability



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## HIGHLIGHTS

- The effect of superpermeability is suggested for Direct Internal Recycling (DIR).
- The influence parameters on superpermeability are outlined.
- Superpermeability was employed for pumping with a compression ratio of 70.

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## ABSTRACT

The effect of superpermeability is capable of separating hydrogen and its isotopes out of gas mixtures at low pressures even against a pressure gradient. This process allows strongly enhanced permeation. It relies on metal membranes that are exposed to atomic hydrogen. If the chemisorption on its surface is inhibited, the atomic hydrogen can still enter the bulk, but hydrogen recombination on the surface is suppressed. This is an ideal concept for the implementation of Direct Internal Recycling (DIR) in future fusion machines in order to minimize the device tritium inventory. In this publication the influence parameters on superpermeation are outlined. Additionally, permeation measurements are shown and interpreted which were performed in the HERMES facility at KIT. During the measurements a change of the surface properties was found.

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## 1. Introduction

Besides the scarce resources of tritium also safety issues demand an intelligent design for any setup with tritium. Especially the development of the fusion fuel cycle of a fusion power plant such as DEMO has to apply the “as low as reasonable achievable” (ALARA) – principle on the tritium inventory. This is the motivation for the development of Direct Internal Recycling (DIR). This concept tries to decrease the inventory by separating most of the hydrogen from the exhaust gases in a system with small residence time close to the torus and feed it back to the fueling system [1]. This hydrogen separation step should be able to work continuously at low pressures. The effect of superpermeation fulfills all criteria demanded for a DIR separation and is thus investigated.

## 2. Superpermeation

Superpermeation was observed the first time in 1938 [2], but only from 1975 [3] it was investigated in detail, especially by Livshits et al. Significant contributions to the underlying processes were also done in Jülich by Waelbroeck et al. [4]. The term “superpermeability” was coined by Livshits for systems with a high likelihood for incident particles to permeate a membrane [5]. It is based on the combination of a metal membrane with high diffusivity with a permeation barrier on the upstream surface that is subjected to an atomic hydrogen flux. This leads to drastically enhanced permeation.

### 2.1. Hydrogen permeation

The process of permeation of hydrogen occurs in various steps that are slightly different for hydrogen molecules and atoms. Hydrogen molecules adsorb on the upstream surface of a membrane by dissociative chemisorption, breaking the molecule into atoms. The activation energy for the chemisorption presents a high energy barrier for molecules. Atomic hydrogen does not need to

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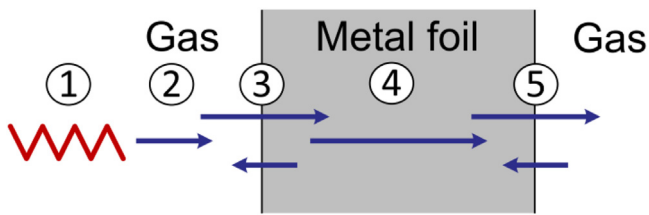


Fig. 1. Relevant locations of process steps for superpermeation.

dissociate anymore and thus has a much lower activation barrier, it absorbs easily. The next steps are the same for incident atomic hydrogen or molecules, as hydrogen is only present in atomic form within the metal. After the adsorption the hydrogen atoms get absorbed into the metal lattice. They move through the membrane by diffusion. On the downstream side they desorb by reemerging to the surface where they can recombine to molecular form with another atom to be able to leave into the gas phase. At temperatures below 1000 K the hydrogen desorbs only as molecules [6].

## 2.2. Process steps of a superpermeable setup

In Fig. 1 the areas of interest of the various process steps for superpermeation are shown and numbered. First atomic hydrogen has to be produced. It will be transported to the metal foil, where ad- and absorption as well as desorption on the upstream surface occurs. It can move through the metal bulk. The hydrogen on the back surface can leave into the gas phase by recombination into molecules, but of course re-adsorption is also possible.

The production of atomic hydrogen is often done by an incandescent metal wire. Although this is easily achievable, this method has a number of drawbacks. Besides the high temperature that causes limited lifetime and sputtering of the wire this method becomes increasingly ineffective at pressures above  $10^{-5}$  Pa [6]. As alternatives various plasma configurations are in discussion such as the electron cyclotron resonance plasma used in the experiment of this paper.

The transport between the hydrogen source and the metal foil is extremely dependent on operating pressure and the geometric arrangement of the setup.

Normally hydrogen membranes are operated in the diffusion-limited regime as this gives an upper limit to the hydrogen flux that can permeate a membrane. But as superpermeation relies on a surface barrier, it is a special case of surface-limited permeation. The rate determining step for surface limited permeation is the dissociative chemisorption of the hydrogen molecules. The likelihood of an incident molecule to adsorb on the surface is much smaller than of atomic hydrogen. If atomic hydrogen is present, its flux to the surface will govern the permeation process.

Although the process is governed by the surface, the diffusivity still is very important. The diffusion needs to be much quicker than the surface processes in order not to become the rate determining step. The diffusion activation energy  $E_D$  is always positive. This results in a rise of diffusivity  $D$  towards higher temperatures, as can be seen from Eq. (1). This gives a minimum operation temperature for a superpermeable membrane.

$$D = D_0 \exp \left\{ \frac{-E_D}{kT} \right\} \quad (1)$$

The processes on the downstream side are the reverse as in without the presence of atomic hydrogen in the gas phase.

Fig. 2 shows superpermeation in an idealized way. The energy barrier on the upstream side is a result of a non-metal film on the surface. In vacuum, a hydrogen molecule has to overcome its binding energy in order to split up. The necessary energy is considerably

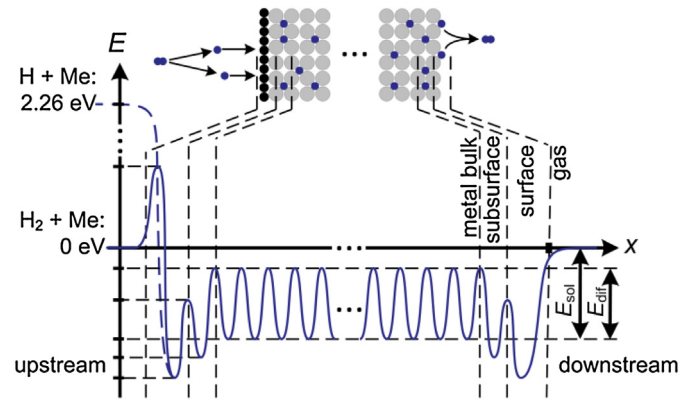


Fig. 2. Idealized potential energy diagram for hydrogen passing a superpermeable metal foil.

lowered in the presence of metals, as their valence electrons can assist this process. This catalytic behavior can be shielded by non-metal films such as oxides. The figure shows a material with a negative heat of solution ( $E_{sol}$ ) such as vanadium which is also used in the experiment of this paper.

If one relies on “natural” surface layers such as oxides, it is unlikely that there is only a surface layer on the upstream side. In this case of equal surface layers on both sides, the membrane will gather a high internal concentration of hydrogen that will leave the membrane towards both sides.

The amount of hydrogen within the metal foil depends on its volume and the solubility of hydrogen. The solubility  $S$  can be described by an Arrhenius ansatz like in Eq. (2):

$$S = S_0 \exp \left\{ \frac{-E_{sol}}{kT} \right\} \quad (2)$$

In contrast to the diffusivity, the activating energy of the process  $E_{sol}$  can be either positive or negative. A temperature rise will increase the solubility for metals with an endothermic solution process such as iron and decrease for metals with an exothermic solution process such as vanadium.

The stability of a surface layer can also change with temperature. This is valid both for non-metal layers as used by Livshits as well as the approach by the group of Waelbroeck that employed metal membranes covered with a second metal [7]. In the latter case, an increased temperature can limit the lifetime of such a membrane as diffusion will lead to mixing of the layers. Changes in the crystal structure and the formation of hydrides with the used metal(s) also have to be taken into account. If hydrides are formed, they will lead to foil embrittlement and possibly foil fracture. Fig. 3 shows the phase diagrams of vanadium with the three hydrogen isotopes. The  $\alpha$ -phase is the only stable one for temperatures above  $200^\circ\text{C}$ . This avoids excessive stress on the membrane, although the metal lattice still gets widened by the hydrogen.

## 2.3. Features of superpermeation

There are two significant features of superpermeation in the following experiments that can be derived from the previously described process steps.

The enhanced permeation is probably the most striking feature. In the case of superpermeation the pressure on the back surface of the membrane can exceed the pressure on the front. This compression is not possible for any system with incident molecules. The maximum compression is dependent on the energy barrier on the front surface of the membrane. In theory the degree of compression can become as high as  $10^{10}$  [10].

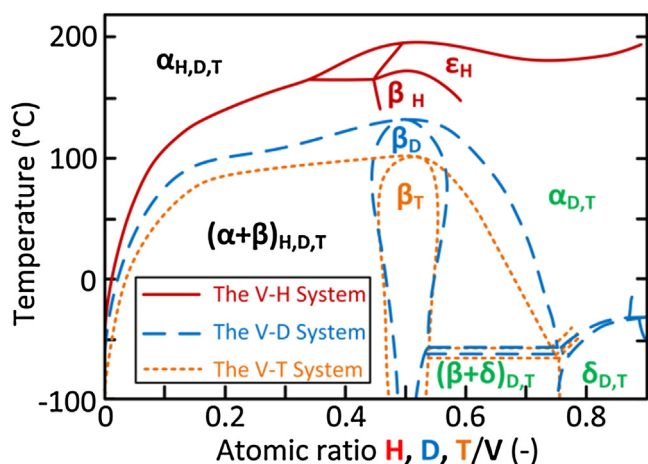


Fig. 3. Hydrogen-Vanadium phase diagram for all three hydrogen isotopes, protium (H), deuterium (D) and tritium (T), data from Refs. [8] and [9].

If the pressure on the back side of the membrane is much lower than the maximum pressure, the permeating flux is totally governed by the incident atomic hydrogen. For stable conditions on the front of the membrane, the permeating flux should be constant. This results in a linear pressure increase during the experiment.

### 3. Experiment

#### 3.1. HERMES setup

At KIT, the Hydrogen Experiment for Research on METal foils and Superpermeability (HERMES) has been set up. It consists of two vacuum chambers that are separated by a metal foil. One chamber is equipped with an electron cyclotron resonance (2.45 GHz, GenII by tectra) plasma source. Both chambers are separately pumped and the pressure is determined by various gauges. A schematic layout of HERMES can be seen in Fig. 4.

#### 3.2. Measurement procedure

Measurements are performed by establishing constant conditions in the upstream chamber and at the metal foil. Most important are the metal foil temperature and the upstream hydrogen gas pressure, which is controlled by a mass flow controller. The turbomolecular pump was constantly running. The downstream chamber is meanwhile evacuated to pressures in the  $10^{-5}$  Pa region. The measurement is started by closing a gate valve between the turbo molecular pump and the downstream chamber. The pressure rise in this chamber holds the information about the permeated hydrogen flux. A gas-driven permeation without the plasma source is conducted before each superpermeation measurement in order to prove the integrity of the metal foil and get qualitative information on the surface condition of the foil. For the presented experiments an industrial grade vanadium foil with a thickness of  $100 \mu\text{m}$  was used.

#### 3.3. Compression experiment

During the experiment the foil had a temperature of about  $290^\circ\text{C}$  with slight variations during the experiment. The plasma source was running during the whole experiment. The upstream pressure was constant at 2 Pa, as can be seen in Fig. 5. The measurement is started by closing the gate valve and a pressure rise in the downstream chamber can be observed. The pressure rise is nearly linear during the course of the nine hours of the experiment

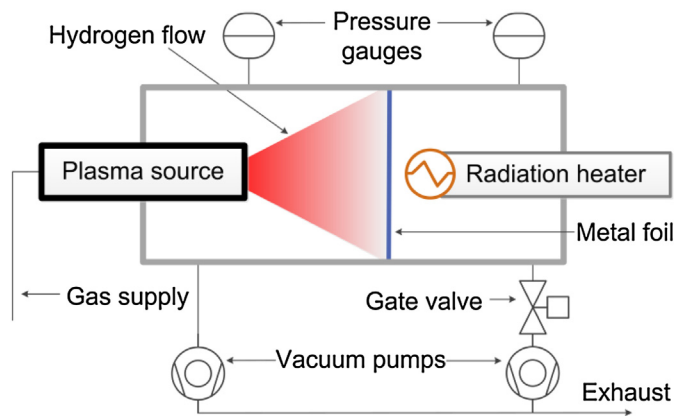


Fig. 4. The HERMES Setup at KIT.

and reaches a pressure of 140 Pa. This gives a compression factor of 70. The pressure rise in the downstream chamber can be used to calculate the pumping speed of the membrane. This pumping speed is roughly constant for the whole nine hours. A slight sabre-tooth variation can be seen. The origin of these variations is not yet explained.

This measurement features the expected behavior for superpermeation. The pressure in the downstream chamber has risen above the upstream value very quickly (7:40 min) after the start of the experiment. Nevertheless it continues nearly linearly, which is another feature expected in the case of superpermeation.

#### 3.4. Change of surface layers

A common problem for measurements relying on a surface energy barrier properties is their stability [11]. This gave the motivation for a measurement probing this feature.

Fig. 6 shows five consecutive gas driven permeation experiments with the same vanadium foil as in the previous experiment. Once again the pressure rises in the downstream chamber are shown. In these measurements they are in the mPa region. The upstream pressure was again 2 Pa during the experiment. After an initial quick rise, which could be caused by the closing gate valve, a nearly linear pressure rise is established in each of the measurements. At 1 mPa a step in the pressure rise can be observed. This is a feature of the used pressure sensor.

The four dotted lines display the pressure rise of four consecutive gas driven permeation experiments. The experiment with the weakest pressure rise was performed first. Each of the following had a steeper rise. After the four measurements a plasma experiment was performed (PDP). It is not shown here. Afterwards a fifth gas driven experiment was done, its pressure rise is shown with the solid line.

The pressure rise to higher values in the same amount of time show that more hydrogen permeated through the membrane. The plasma driven permeation experiments revealed surface limited hydrogen permeation. Thus the increased permeation has to be caused by a decreasing surface barrier. It consists of a natural oxide layer. Livshits previously reported that surface barriers will rebuild themselves when the mobility of dissolved oxygen in the metal is increased [12]. The diffusivity of oxygen in vanadium has increased due to the higher foil temperature during the plasma driven permeation.

### 4. Conclusion and outlook

The effect of superpermeation was used to demonstrate its capability as a hydrogen vacuum pump. Hydrogen was compressed by a

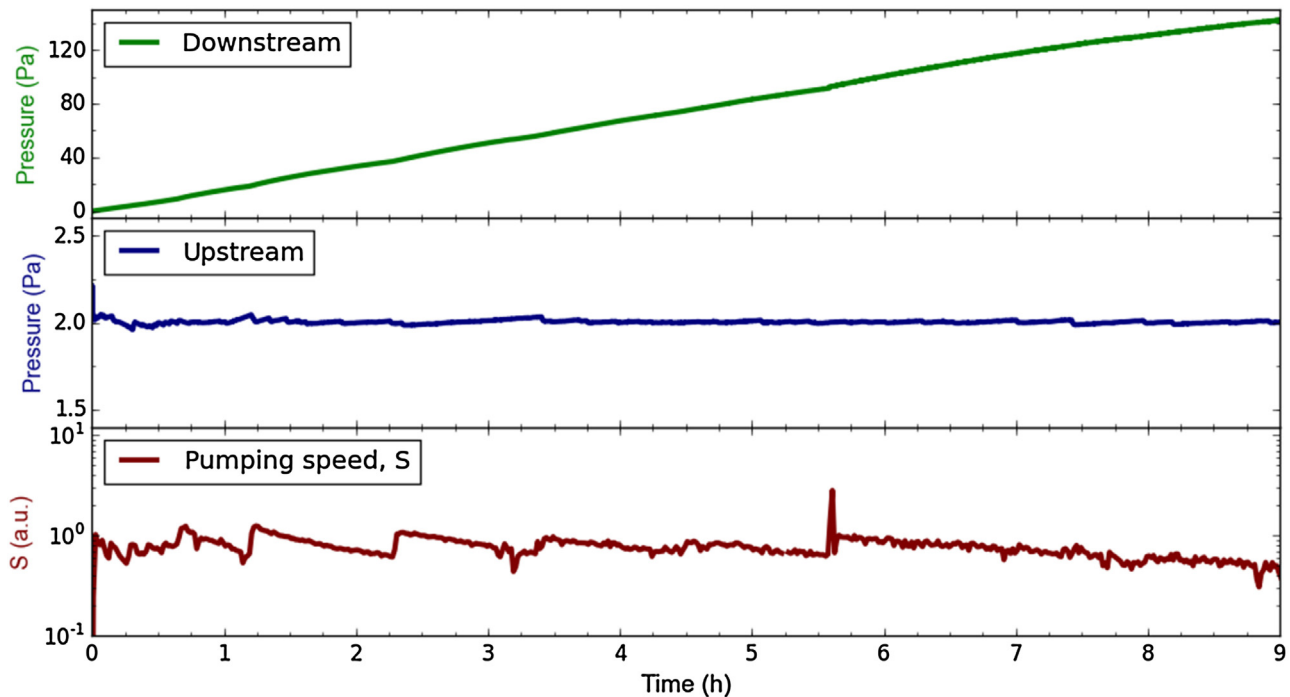


Fig. 5. Superpermeation test in HERMES of a vanadium membrane with natural oxygen surface layers.

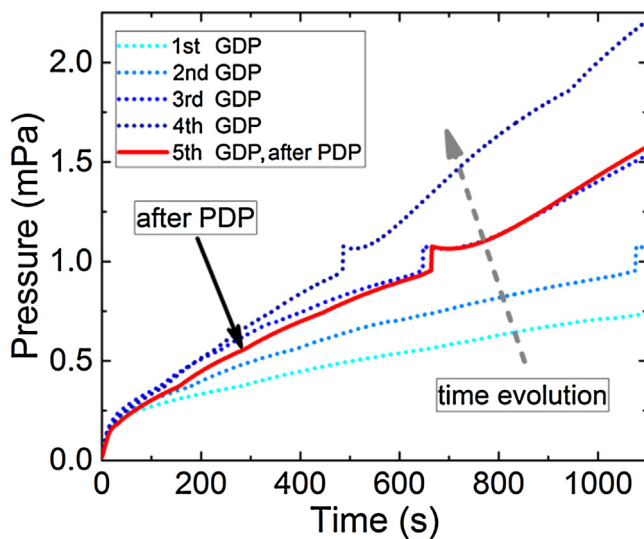


Fig. 6. Measurements of gas driven permeation (GDP) in HERMES.

factor of 70. A change of the metal surface properties was observed and presented. The relevant influence factors for superpermeation were pointed out. This gives the basis for future experimental and theoretical studies that will be conducted at KIT. It was proven, that Direct Internal Recycling (DIR) can be based on a unit relying on superpermeation.

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