Measurement and modeling of hydrogen transport through high-flux Pd membranes

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Abstract

The permeability of H\textsubscript{2}-selective palladium membranes fabricated with microsystem technology has been studied. The permeation experiments have been carried out at temperatures between 623 and 873 K at H\textsubscript{2} feed partial pressures of 0.2–1.0 bar. At 823 K, a permeance based on the free membrane area of 18 mol H\textsubscript{2}/m\textsuperscript{2} s bar\textsuperscript{0.58} has been measured for a Pd membrane with a thickness of 0.5 \textmu m. From the permeation experiments the rate determining transport step and the stability of the membranes have been determined. At 873 K the H\textsubscript{2}/He selectivity decreases rapidly, indicating the formation of pinholes at higher temperatures. From a combination of experiments and computer simulations the limiting transport step has been determined to be H-atom diffusion through the membrane at elevated temperatures and H\textsubscript{2} surface reactions at the retentate side at lower temperatures.

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Keywords: Hydrogen permeation; Steam activation; Microsystem technology; Limiting transport step; Surface contamination

1. Introduction

In the last decade a large increase in the H\textsubscript{2} flux of Pd and Pd alloy membranes has been achieved by reducing the membrane thickness using porous materials such as alumina or sintered steel as support of the membrane. Microsystem technology enables the fabrication of membranes with a thin support layer (about 1 \textmu m) or even without support [1–3]. The absence of the porous support layer substantially reduces the mass transfer resistance and hence a dramatic increase of the H\textsubscript{2} flux can be achieved [4,5]. The well defined surface of free membrane area makes these membranes very well suited for studies of the prevailing transport mechanism.

In previous papers, we have presented the flux characterization of Pd membranes fabricated with microsystem technology over a temperature range of 623–723 K [4,6]. The measured H\textsubscript{2} flux is higher than literature values for membranes of comparable thickness deposited on a porous support, however, it appears to be approximately 20\% of the flux calculated with the model proposed by Ward and Dao [7]. It also appears that the measured flux is not only limited by diffusion through the membrane but also by H\textsubscript{2} surface reactions due to contaminations. In the present paper, the membrane has been activated with steam, which will remove adsorbed carbon species from the Pd surface and will thus increase the availability of sites for the dissociative adsorption and associative desorption of H\textsubscript{2}.

In the literature, the rate-limiting step is often determined by fitting measured data to the following equation:

\[ J_\text{H}_2 = \Pi(T) (P_{\text{H}_2, \text{ret}}^{\text{n}} - P_{\text{H}_2, \text{perm}}^{\text{n}}) \]  

(1)

in which \( J_\text{H}_2 \) is the H\textsubscript{2} flux, \( \Pi(T) \) the permeance, \( P_{\text{H}_2, \text{ret}} \) and \( P_{\text{H}_2, \text{perm}} \) are the H\textsubscript{2} partial pressure at the retentate side and the permeate side, respectively, and the exponent \( n \) is a parameter which value depends on the limiting transport mechanism. If H\textsubscript{2} surface reactions at the permeate side limit the flux then \( n = 0 \). If diffusion through the membrane limits the flux then \( n = 0.5 \) and if gas phase resistance or surface reactions at the retentate side are limiting the flux, \( n \) becomes unity. In the present study, the value of \( n \) and \( \Pi \) are determined in two ways. First, the H\textsubscript{2} feed partial pressure and the H\textsubscript{2} partial pressure of the permeate outlet are fitted to Eq. (1). Second, a theoretical model of the membrane module is used to determine the local partial

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H₂ pressures and fluxes along the membrane which are used in the fitting procedure. Furthermore, the stability of the membranes has been studied by monitoring the selectivity during the permeation experiments.

2. Experimental

2.1. Membrane preparation and packaging

Two types of Pd membranes were prepared as described previously [1,8]. One type of Pd membrane was prepared without support, called ‘free-hanging membrane’, and the other type was prepared on top of a 1.3 μm thick microsieve of low stress silicon rich nitride and silicon oxide.

The first module contained a free-hanging membrane with a thickness of 0.9 μm, packaged between two borosilicate glass plates as shown schematically and described in more detail in a previous paper. The borosilicate plates were designed to force the feed gasses to pass through the apertures in the silicon wafer [6]. To allow measurements at temperatures above 723 K, the second module consisted of a microsieve-supported membrane of 0.5 μm, packaged between two stainless steel holders (Fig. 1). To compensate for the large difference in thermal expansion of stainless steel and silicon, two graphite rings (Egraflex GTC, 98% graphite, thickness 200 μm) were used as a sealing material between the membrane and the holders. A clamp was applied to fixate the module during gluing and measurements. After applying the clamp, the module was dried at room temperature for 1 h and subsequently the glue was hardened in an oven at 453 K for 2 h. Finally, the module was tested for the presence of leaks by applying 100 mbar overpressure.

2.2. Membrane permeation

The H₂ permeability and selectivity of the membranes were determined in the experimental setup as shown in Fig. 2. A known mixture of H₂ and He was flushed continuously through the retentate side and nitrogen through the permeate side. Mass flow controllers regulated all gas flows. The retentate pressure was regulated slightly above atmospheric pressure by a back-pressure controller and the permeate outlet was not restricted and was therefore at atmospheric pressure. The gas flows were heated by a spiral that was placed in the same oven as the membrane module. Steam to activate the membrane was produced by evaporating water supplied by a high-pressure liquid chromatography pump. The liquid flow rate of the pump determined the steam flow. The water evaporation took place in a stainless steel spiral with inner diameter of 0.8 mm and length of 1.5 m, placed inside the same oven. The permeate composition was measured by means of a micro gas chromatograph (Varian CP4900), equipped with a molsieve 5 Å column and thermal conductivity detector (TCD). Argon was used as the carrier gas, which made the TCD highly sensitive to He and H₂. The gasses were 99.999 vol% pure.

After placing the membrane module in the system, He was fed to the retentate and N₂ to the permeate. A small positive transmembrane pressure was applied to detect possible pinholes in the membrane layer by measuring the presence of He in the
Fig. 3. Schematic view of the stainless steel module as it is modelled: (a) cross-section in the flow direction, (b) actual configuration of the rows of apertures and (c) model configuration of a simplified column of apertures.

Table 1
Parameters used in the simulations of the modules

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Stainless steel module “micosieve-supported”</th>
<th>Borosilicate module “free hanging”</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane area (mm$^2$)</td>
<td>3.3</td>
<td>8.8</td>
</tr>
<tr>
<td>Membrane thickness (μm)</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>Gas duct width (mm)</td>
<td>18</td>
<td>18 (permeate side)</td>
</tr>
<tr>
<td>Gas duct length (mm)</td>
<td>23</td>
<td>14 (permeate side)</td>
</tr>
<tr>
<td>Gas duct height (mm)</td>
<td>0.2</td>
<td>0.2 (permeate side)</td>
</tr>
<tr>
<td>Aperture width (μm)</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>Aperture length (μm)</td>
<td>2000</td>
<td>28</td>
</tr>
<tr>
<td>Aperture height (μm)</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>Number of aperture rows</td>
<td>3</td>
<td>125</td>
</tr>
<tr>
<td>Number of aperture columns</td>
<td>11</td>
<td>8</td>
</tr>
<tr>
<td>Space between apertures columns (μm)$^a$</td>
<td>300</td>
<td>1500</td>
</tr>
<tr>
<td>Correction aperture width at retentate side (μm)$^a$</td>
<td>113</td>
<td></td>
</tr>
<tr>
<td>Correction aperture width at permeate side (μm)$^a$</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>Fraction membrane area (membrane/microsieve)$^b$</td>
<td>0.0833</td>
<td>1</td>
</tr>
<tr>
<td>Activation energy of the associative desorption (kJ/mol H$_2$)</td>
<td>46.0</td>
<td>46.0</td>
</tr>
</tbody>
</table>

Operational conditions are equal to the experiments. The values of the physical parameters in the membrane model are equal to the values presented by Ward and Dao [7] if no further changes are remarked.

$^a$ Extra width to include the mass transfer exchange between the area above the membranes and between the apertures, based on $Fo = 1$ (see Appendix A) for a single column of apertures.

$^b$ Porosity is defined as effective membrane area divided by the total aperture area.
If no pinholes were detected, the oven temperature was increased with 3 K/min until the activation temperature of 723 K was reached. Two activation steps with different feed gas mixtures were carried out to compare the influence of H$_2$ activation and steam activation. During the H$_2$ activation step a mixture of 20/80 vol% H$_2$/He was fed to both the retentate and permeate side of the membrane for 4 h. During the subsequent steam activation, a mixture of 20/20/60 vol% steam/H$_2$/He was fed to the retentate side and N$_2$ to the permeate side for 72 h. To measure the effect of steam activation, series of permeation experiments with varying H$_2$ concentration in the feed were carried out before and after activation. The H$_2$ partial pressure in the feed was varied from 0 to 1.01 bar at temperatures of 623, 673, 723, 823 and 873 K, respectively.

After the permeation experiments the membrane surface was inspected and the membrane thickness was confirmed using a scanning electron microscope (SEM, Jeol JSM-5600).

3. Model description

In order to determine which transport step is limiting the H$_2$ flux in the permeation experiments, a one-dimensional model has been developed. The model calculates local driving forces for mass transfer inside the module, which depend on the module type used (see Fig. 3 and Table 1 for details).

The flows of the retentate and permeate are co-current. As a consequence, the H$_2$ concentrations and the driving force for mass transport through the membrane will change in the flow direction. The flow channel inside the graphite sealing is wider than the width occupied by the membrane surface, hence 50% of the feed and sweep gas will bypass the membrane (Fig. 3b and c). This effect is taken into account in the model by creating two zones for each membrane side: a membrane zone and a bypass zone. The gas flowing through the bypass zone had no exchange with the membrane; a minor exchange taking place between the gas streams in the two zones at the same side of the wafer is described in Appendix A. In the membrane zone the H$_2$ transport in the gas phases in the direction perpendicular to the membrane is described by several mass transfer coefficients in series (see Appendix A). Mass transport through the membrane is described according to the model of Ward and Dao [7], which takes into account the following steps: dissociative adsorption, surface to the Pd bulk transition, diffusion through the Pd bulk, the Pd bulk to the surface transition, and associative desorption. The quasi-chemical equilibrium approximation is used to describe the probability of two adjacent empty hydrogen adsorption sites. For the activation energy of the associative desorption a value of 46 kJ/mol H$_2$ is used; the values of the other parameters are taken from [7].

In Appendix A, the differential equations are presented and the method of solving is indicated. Other parameters used in the simulations are given in Table 1. The outcome of the model calculations will be compared with the experimental flux data in the following section.

4. Results and discussion

First the H$_2$ permeances will be discussed, then the modelling and finally the selectivity and stability of the membrane. The measured H$_2$ fluxes were corrected for the flow through pinholes that developed after some time of operation in the membrane layer, by estimating the H$_2$ flow through the pinholes from the He concentration in the permeate assuming Knudsen diffusion. Fluxes are based on the free membrane area in order to be able to make a comparison with the predictions made by Ward and Dao.

4.1. Effect of steam activation on the H$_2$ permeance

In Fig. 4a and b the effect of the two subsequent activation steps (hydrogen and steam) on the H$_2$ flux at 723 K is given for the two membranes, respectively. In addition, the expected fluxes as calculated with the model are given in the two figures. In

![Fig. 4. The effect of steam activation (20/20/60 vol% steam/H$_2$/He) on the H$_2$ permeation in the 0.9 μm membrane (a) and the 0.5 μm membrane (b). All measurements are carried out at 20/80 vol% H$_2$/He and 723 K. A malfunction in a valve after the first steam activation (a) has caused a drop in the feed flow rate to the module; after approximately 24 h the malfunctioning of the valve was solved, which is visible by the sudden increase in flux.](image-url)
Fig. 4a the H$_2$ flux before steam activation gradually increases, as H$_2$ activation will continue during permeation when H$_2$ is fed to only one side of the membrane. A flux of about 0.7 mol H$_2$/m$^2$/s is reached 140 h after the actual H$_2$ activation step. The first activation with steam induces an increase of the H$_2$ flux, until a stable value of 1.1 mol H$_2$/m$^2$/s is reached after 30 h. A second steam activation does not improve the flux anymore. Steam activation obviously increases the number of free sites for the H$_2$ surface reactions, which are necessary for the permeation through the membrane. As shown in Fig. 4a, the measured fluxes after steam activation are in agreement with the calculated fluxes using the model.

The H$_2$ flux in Fig. 4b is stable after the first H$_2$ activation step. The obtained flux of 1.6 mol H$_2$/m$^2$/s is relatively low as compared to the flux in Fig. 4a when taking into account that the thickness of this membrane is almost half the thickness of the membrane used in Fig. 4a. After steam activation the flux increases to a maximum value of 2.5 mol H$_2$/m$^2$/s, but then decreases to values below the flux before steam activation. This is most likely caused by an increase of the carbon content of the palladium above a critical level where it hampers the H$_2$ surface reactions [10]. We think the carbon stems from pyrolysis products from the glue or gaseous products from reactions between steam or H$_2$ and the glue or the graphite sealing; the methane or carbon oxides formed may react under carbon deposition at the Pd surface. The difference with the 0.9 μm membrane of Fig. 4a is that glue was not present and graphite to a far less extend in the glass bonded module.

4.2. Permeation behavior

In this section the influence of the variation in the H$_2$ feed pressure and temperature on the permeation behavior will be discussed using the H$_2$ partial pressure of the feed $P_{H_2\text{ feed}}$ and $P_{H_2\text{ permeate out}}$.
the permeate outlet \( P_{H_2 \text{perm.out}} \). Obviously this is a simplification, as it neglects the variation of the driving force along the length of the flow path. The experimental values are fitted to Eq. (2), leading to values for \( \Pi(T) \) and \( n \):

\[
J_{H_2} = \Pi(T)(P_{H_2 \text{feed}} - P_{H_2 \text{perm.out}})
\]  

(2)

In Figs. 5 and 6 the measured \( H_2 \) flux versus the driving force is given for the two types of modules at various temperatures. The figures are presented in the same order as the experiments have been carried out. In both figures the corresponding fits of Eq. (2) are given as well. The series with increasing \( H_2 \) feed concentration and decreasing \( H_2 \) feed concentration are fitted separately, and are represented by different symbols. The values of \( \Pi(T) \) and \( n \) (including the values of the standard deviation) obtained by fitting the permeation results are summarised in Table 2.

For the 0.9 \( \mu m \) membrane, the flux at 723 K (Fig. 5a) increases with increasing \( H_2 \) partial pressure in the feed. In the first measurements the obtained fluxes are stable in time. However, 190 h after steam activation (in the figure starting at a driving force of 0.65 bar\(^{0.55}\)) the fluxes start to decrease in time. This decrease in flux is ascribed to contamination of the membrane surface, most likely by carbon. The decrease continues during the series of decreasing \( H_2 \) feed pressures, which results in a value of \( n \) of 1.04. This high value of \( n \) is attributed to a combination of a changing degree of contamination and a shift towards surface limitation at the retentate side. The occurrence of contamination is supported by the fact that a stable and high flux is obtained again after re-activating the membrane with steam and hydrogen. At 673 and 623 K (Fig. 5b and c) the fluxes of the series at increasing and decreasing \( H_2 \) feed pressure are almost equal. For all series the fit describes the measured fluxes well, from which it can be concluded that contamination does not play a role in these measurements. In general the obtained fluxes are very high. Even when these fluxes are translated to values based on the total wafer surface

![Diagram](Fig. 6. \( H_2 \) permeation as a function of the \( H_2 \) driving force between the feed and permeate outlet of the 0.5 \( \mu m \) membrane module at temperatures of 723 K before steam activation (a), 723 K after steam activation (b), and 823 K (c) (in the same order as the experiments).)
Table 2
Fitted parameters $n$ and $\Pi$ of the experimental results and Eq. (2) ($H_2 \uparrow$ = increasing $H_2$ feed partial pressure, $H_2 \downarrow$ = decreasing $H_2$ feed partial pressure). The corresponding values of the standard deviation ($\sigma$) are included.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Temperature (K)</th>
<th>$n$</th>
<th>$\Pi$ (mol H$_2$/m$^2$ s bar$^n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>$\sigma$</td>
<td>Average</td>
</tr>
<tr>
<td></td>
<td>$H_2 \uparrow$</td>
<td>$H_2 \downarrow$</td>
<td>$H_2 \uparrow$</td>
</tr>
<tr>
<td>0.9 $\mu$m</td>
<td>723</td>
<td>0.548</td>
<td>1.044</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>0.490</td>
<td>0.518</td>
</tr>
<tr>
<td></td>
<td>623</td>
<td>0.568</td>
<td>0.499</td>
</tr>
<tr>
<td>0.5 $\mu$m</td>
<td>723</td>
<td>0.815</td>
<td>0.690</td>
</tr>
<tr>
<td></td>
<td>723</td>
<td>1.408</td>
<td>0.710</td>
</tr>
<tr>
<td></td>
<td>823</td>
<td>0.581</td>
<td>0.583</td>
</tr>
</tbody>
</table>

area, values are obtained that exceed the $H_2$ flux of all Pd-based membranes supported by a porous medium reported in the literature.

For the 0.5 $\mu$m membrane (stainless steel module) similar experiments have been performed at temperatures of 723, 823 and 873 K. In Fig. 6a and b, the measured fluxes are given at 723 K before and after steam activation, respectively. From Fig. 6b it can be observed that the flux increases during the measurement at each of the different feed concentrations during the ‘$H_2$ up’ series. This is caused by the preceding steam activation where the time elapsed after the steam activation has been too short to remove all the water from the system [10]. This leads to the extreme value of $n = 1.4$. At 823 K (Fig. 6c) the membrane operation is stable and no difference is found between the two series of measurements. At 873 K the flux has only been determined at 20 vol% $H_2$ in the membrane feed, leading to a value of 4.1 mol H$_2$/m$^2$ s. The measured fluxes are higher for the 0.5 $\mu$m membrane than those measured for the 0.9 $\mu$m one, however, the increase is not proportional. This proves that diffusion in the membrane is not the only rate determining step for the 0.5 $\mu$m membrane in the module with the graphite sealing.

The values of $n$ and $\Pi$, together with their standard deviations are summarised in Table 2. The values of the standard deviations are high for values of $n > 1.0$, indicating that changes occurred during these series, like a change in water adsorption (Fig. 7b) or in surface contamination (Fig. 5a) or in surface morphology [11]. Series with values for $n < 1.0$ show small standard deviations; the values close to $n = 0.5$ suggest that hydrogen diffusion through the membrane limits the flux. Additionally, activation energies have been calculated (Table 3). It has been shown in the literature that values of about 12 kJ/mol H$_2$ correspond with a diffusion limited permeation [7,12,13]. However, especially for lower temperatures we calculate significantly higher values (between 30 and 50 kJ/mol H$_2$), indicating that processes occurring at the surface become important. Obviously, for the lower temperature ranges, the values for $n$ and the activation energy are not consistent. In the following paragraph, the $H_2$ permeance has been modeled in order to gain more insight in the underlying phenomena.

Fig. 7. The experimental ($H_2$ up and $H_2$ down) and calculated fluxes are compared for: (a) 0.9 $\mu$m membrane and (b) the 0.5 $\mu$m membrane. The values used for $n$ in the driving force (both for experimental and model results) are those from the simulations given in Table 5. For clarity the experimental data in which steam still influenced the flux are omitted in b.
4.3. Modeling of the H₂ permeance

Model simulations are carried out for the input conditions (feed composition and temperature) of all experiments without using experimental output like outlet concentrations or H₂ fluxes. The obtained simulation results are local and outlet concentrations and fluxes. Four different definitions of the driving force (Table 4) have been used to calculate values of \( n \) and \( \Pi \), fitting Eq. (1) to the model results.

The calculated fluxes and the experimental fluxes are compared in Fig. 7a and b for both modules, respectively. The values for \( n \) and \( \Pi \) obtained from the fit of the simulation results are given in Table 5. From Fig. 7a it can be seen that the measured fluxes of the 0.9 \( \mu \)m membrane are up to about 20% lower than the calculated fluxes. The experimental and simulation results of the 0.5 \( \mu \)m membrane (Fig. 7b) agree rather well, but at 723 K the measured fluxes are almost 50% lower. The observed differences are most likely due to the fact that the model does not account for contamination effects, as will be discussed later.

In Fig. 8 the values of \( n \) are given as a function of temperature for the four fits of the simulation results. Also the values fitted from the experimental permeation results are given. For the simulations of both module types (Fig. 8a and b, respectively) it can be seen that upon an increase in temperature, a shift in the transport limitation occurs from partly associative desorption limited to a limitation by diffusion in the membrane (from \( n \geq 0.3 \) to 0.5 for the local and surface based description). From the small difference in \( n \) in the ‘local’ series compared to the ‘surface’ series, it can be concluded that mass transfer in the gas phase hardly causes extra resistance due to the small height of the gas ducts in the module. As expected, the value of \( n \) of the diffusion-based fit is constant (\( n = 1 \)) for all temperatures.

A clear difference exists between the values of the ‘local’ and the ‘average’ series, although the trend is comparable. The value of \( n \) of the ‘average’ series increases to values of above 0.7, while the rate limiting transport step is still H-atom diffusion through the membrane (\( n = 0.5 \) ‘local’). Due to the definition used for the driving force in the ‘average’ series we can conclude that bypassing of gas in the modules results in a value of \( n \) that does not correspond with the underlying transport limitation.

The values found for \( n \) in the measurements can be compared to the \( n \) values of the simulation calculated with the fit ‘average’. Without the model description, the experimental values could be interpreted as a constant value for \( n \) of about 0.5, leading to the conclusion that transport is diffusion limited. However, the model clearly indicates that \( n \) should decrease upon a decrease in temperature. From the difference in trends it can be concluded that the shift of limiting steps in the experiments is not the same as in the simulations. The trend found for \( n \) in the experiments corresponds with a shift in transport limitation from surface reactions at the retentate side to surface reactions at the permeate side or diffusion through the membrane. This has also been observed in Fig. 7. Also the experimentally found values for the activation energy support the suggestion that contamination of the surface limits the H₂ transport at lower temperatures.

### 4.4. Selectivity and stability of the membrane

For more than 65 days no helium has been detected in the permeate during the measurements with the 0.9 \( \mu \)m membrane.

#### Table 4

<table>
<thead>
<tr>
<th>Model</th>
<th>Flux H₂</th>
<th>Driving force variable</th>
<th>Driving force variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 &quot;average&quot;</td>
<td>Average flux of the complete module</td>
<td>( P_{H₂\text{ret}}^{\text{in}} )</td>
<td>( P_{H₂\text{perm}}^{\text{out}} )</td>
<td>H₂ partial pressure of the feed and permeate out, respectively</td>
</tr>
</tbody>
</table>
| 2 "local"  | Local flux of one grid cell | \( P_{H₂\text{ret}}^{\text{in}} \) | \( P_{H₂\text{perm}} \) | Local H₂ partial pressure in the gas bulk of the membrane zone
d
| 3 "surface" | Local flux of one grid cell | \( P_{H₂\text{ret}}^{\text{in}} \) | \( P_{H₂\text{perm}} \) | Local H₂ partial pressure at the membrane surface
d
| 4 "diffusion" | Local flux of one grid cell | \( (\text{H/Pd})_{\text{ret}}^{\text{in}} \) | \( (\text{H/Pd})_{\text{perm}} \) | H/Pd ratio in the bulk Pd just below the surface
d

\( ^a \) In the fit procedure, the local H₂ concentrations at two positions in the module have been used: the first and the last grid cell where Pd is present in the module.

#### Table 5

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Temperature (K)</th>
<th>( n )</th>
<th>( \Pi ) (mol H₂/m² s bar⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average</td>
<td>( \sigma )</td>
</tr>
<tr>
<td>0.9 ( \mu )m</td>
<td>723</td>
<td>0.702</td>
<td>0.028</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>0.613</td>
<td>0.028</td>
</tr>
<tr>
<td></td>
<td>623</td>
<td>0.476</td>
<td>0.031</td>
</tr>
<tr>
<td>0.5 ( \mu )m</td>
<td>723</td>
<td>0.612</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>0.517</td>
<td>0.024</td>
</tr>
<tr>
<td></td>
<td>623</td>
<td>0.325</td>
<td>0.039</td>
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<tr>
<td></td>
<td>823</td>
<td>0.669</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>873</td>
<td>0.710</td>
<td>0.012</td>
</tr>
</tbody>
</table>

\( ^a \) As a result of contamination the flux at higher temperature is lower and causes the activation energy to be negative.
Fig. 8. Values of the exponent \( n \) found for the 0.9 \( \mu \)m membrane (a) and the 0.5 \( \mu \)m membrane (b) by fitting Eq. (1), to the modelling results. Standard deviation indicated by bars. The numbers (1–4) represent the different definitions of the driving force as given in Table 4.

Table 6
The selectivity and temperature history of the membranes

<table>
<thead>
<tr>
<th>0.9 ( \mu )m membrane</th>
<th>0.5 ( \mu )m membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (days/h)</td>
<td>Temperature (K)</td>
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<td>22/3</td>
<td>823</td>
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\(^a\) The membrane feed was pure He; no helium was detected at the permeate side. The detection limit is approximately 0.01 vol% He in N\(_2\).

Fig. 9. Rapid increase of the He flow through the 0.5 \( \mu \)m membrane at 873 K.
After the temperature change from 673 to 623 K, however, the \( \text{H}_2/\text{He} \) selectivity is 60 at a \( \text{H}_2/\text{He} \) feed ratio of 20/80 (Table 6). From then on the hydrogen selectivity remains constant. At the start-up of the 0.5 \( \mu \text{m} \) membrane also no helium has been detected in the permeate, which changes after the activation step. The selectivity is 200 at a \( \text{H}_2/\text{He} \) feed ratio of 20/80. As the value of \( n \) for He equals unity and is below unity for \( \text{H}_2 \), the selectivity is concentration dependent. At 823 K, the helium flow through the membrane starts to increase and the selectivity drops to values of 60–40. At 873 K the selectivity drops gradually and becomes unity after several hours (Fig. 9).

The total operation time under varying hydrogen feed concentrations and temperatures has been 2000 and 540 h for the 0.9 and 0.5 \( \mu \text{m} \) membrane, respectively. SEM micrographs of the membrane after the permeation experiments show that irregularly shaped openings have been formed in the Pd layer at the openings of the microsieve (Fig. 10). A closer look at the membrane reveals that the structure of the Pd has changed from a smooth surface without pin-holes (Fig. 10a) into a grain-structured surface (Fig. 10b), probably due to a combination of temperature-annealing and the effects of hydrogen. The size of the grains is between 0.1 and 1 \( \mu \text{m} \). Grain growth induces the membrane to become locally thinner, eventually leading to the formation of holes (Fig. 10c). Comparable results have been shown in a recent article for palladium–copper membranes[14].

5. Conclusions

The permeability of \( \text{H}_2 \)-selective palladium membranes fabricated with microsystem technology has been studied. From the permeation experiments the rate determining transport step and the stability of the membranes have been determined. At 823 K, a permeance of 17.7 mol \( \text{H}_2/\text{m}^2 \text{s bar}^{0.58} \) has been measured for a Pd membrane with a thickness of 0.5 \( \mu \text{m} \).

From the difference in trends of the flux versus temperature found in the simulations and in the experiments, it can be concluded that at lower temperatures the transport limitation in the experiments is due to surface reactions at the retentate side rather than at the permeate side. With increasing temperature, the flux starts to become limited by H-atom diffusion through the membrane or by surface reactions at the permeate side. At higher temperatures the experimental and calculated fluxes are in good agreement.

From the results of the model it can be concluded that the method of calculating \( n \) in previous papers has resulted in values of \( n \) larger than expected based on the limiting transport step only; this is due to the presence of a bypass stream and a varying driving force along the flow path in the module.

The membranes have shown to be stable for a rather long period, however, SEM analysis shows the formation of a grain-structured surface. At 873 K the \( \text{H}_2/\text{He} \) selectivity decreases rapidly, caused by the formation of holes at higher temperatures.

Acknowledgements

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Appendix A

For the description of mass transfer in the modules used, the following mathematical description has been made. Both in the membrane zone and in the by-pass zone concentration gradients are assumed to be absent in the \( y \)-direction (perpendicular to
the flow but parallel to the membrane). Mass transport between the streams in the two zones occurs by convection due to the change in the gas flow rates caused by the H2 transfer through the membrane. To compensate for the diffusive transport in the y-direction, the width of the membrane zone is extended with a characteristic length calculated from the Fourier number (Fo). The characteristic time in Fo is the gas residence time in a single grid cell and the value of Fo is set to one. In the flow direction (x-direction) the convective and diffusive mass transport are taken into account.

The transport of H2 through the membrane module at the retentate side in the membrane zone can be described by

\[
\frac{\partial c_t}{\partial t} = D(c_t, T, P) \frac{\partial^2 c_t}{\partial x^2} - \frac{\partial u_t c_t}{\partial x} + \frac{J(c_t, c_p, T)\varepsilon}{h_t}
\]

(\ref{eq:1})

where \( c_t \) is the concentration of H2 at the retentate side in the membrane zone, \( D \) the diffusion coefficient, \( T \) the temperature, \( P \) the pressure, \( u_t \) the gas velocity in the x-direction, \( J \) the molar H2 flux through the membrane, \( \varepsilon \) the fraction of the membrane zone occupied by effective membrane area, \( w_{k,b} \) the total width of the by-pass zone, \( t \) an Eulerian time, \( x \) a spatial coordinate, \( h_t \) the height of the gas duct at the retentate and \( w_i \) is the total width of the duct. The transport in the bypass zone at the retentate side can be described by

\[
\frac{\partial c_{t,b}}{\partial t} = D\left(c_{t,b}, T, P\right) \frac{\partial^2 c_{t,b}}{\partial x^2} - \frac{\partial u_{t,b} c_{t,b}}{\partial x} + c_{t,b} \frac{\partial u_t}{\partial x}
\]

(\ref{eq:2})

The change of velocity \((u_{t,b} = u_t)\) caused by the removal of H2 is given by

\[
\frac{\partial u_t}{\partial x} = -\frac{J(c_t, c_p, T)\varepsilon RT}{h_t P}
\]

(\ref{eq:3})

where \( R \) is the gas constant and \( P \) is the total pressure. The influence of the pressure drop can be neglected. The transport at the permeate side is described by similar equations in which the \( p \) in the permeate side is replaced by \( c_p \) in the retentate side:}

\[
\frac{\partial c_p}{\partial t} = D\left(c_p, T, P\right) \frac{\partial^2 c_p}{\partial x^2} - \frac{\partial u_p c_p}{\partial x} + \frac{J(c_t, c_p, T)\varepsilon}{h_p}
\]

(\ref{eq:4})

\[
\frac{\partial c_{p,b}}{\partial t} = D\left(c_{p,b}, T, P\right) \frac{\partial^2 c_{p,b}}{\partial x^2} - \frac{\partial u_{p,b} c_{p,b}}{\partial x} + c_{p,b} \frac{\partial u_p}{\partial x}
\]

(\ref{eq:5})

\[
\frac{\partial u_p}{\partial x} = \frac{J(c_t, c_p, T)\varepsilon RT}{h_p P}
\]

(\ref{eq:6})

The flux \( J(c_t, c_p, T) \) is calculated with the model proposed by Ward and Dao and three mass transfer coefficients. The mass transfer coefficients in the gas ducts at the retentate and permeate side are calculated using a Nusselt number that is valid for the applied geometry and flow regime [15]. The third mass transfer coefficient describing H2 transport through the stagnant gas layer in the aperture is defined as the ratio of the aperture height and the H2 diffusion coefficient. The effect of the net flux (Stefan diffusion) is taken into account for all three cases.

The obtained system of four partial differential equations (PDE) and two ordinary differential equations (ODE) are solved with the method of lines [16] and the fourth-fifth order Runge–Kutta method. The grid of the model is examined by doubling the number of cells in the x-direction and comparing the obtained results.

Two differences between the glass and the stainless steel module made it necessary to adjust the model. First, at the retentate side of the glass module the gas flow is forced through the apertures, hence the mass transfer resistance in the gas phase will be smaller and no bypassing of gas occurs at this side. Second, the apertures are rotated 90° with respect to permeate flow and thus a cross flow configuration is created. To accommodate for this, an average H2 concentration in the retentate has been applied to create a mathematical link between retentate and permeate.

References


