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High-Flux Palladium Membranes Based on Microsystem Technology

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Hydrogen-selective Pd membranes can be used to improve the conversion of dehydrogenations, steam reforming, and the water gas shift reaction. The application of these membranes on a large scale is prohibited by the costs of the existing membranes, requiring membranes with a much higher permeability. In this paper we describe the manufacturing of Pd and Pd/Ag membranes using microsystem technology. These membranes exhibit fluxes that can be a factor of 10 higher than the fluxes obtained using porous supports. Despite the thin Pd and Pd/Ag layers applied, these membranes are pinhole-free.

Introduction

In many reports the application of H_2-selective membranes has been studied to improve dehydrogenation reactions, steam reforming of methane or the water gas shift reaction.[1−4] In these processes the single-pass conversion can significantly be increased by removing H_2 from the reaction zone. Additionally, process conditions can often be set milder while the same conversion is maintained, thus reducing the formation of byproducts. Application of H_2-selective palladium membranes on a large scale is rather expensive, and a cost reduction is mandatory to make this technology economically feasible.[5] Obviously, increasing the H_2 flux while the selectivity is kept high reduces the required membrane surface area and therefore the membrane investment costs. To increase H_2 fluxes it will be necessary to reduce the thickness of the membrane and/or to increase the permeability of the porous support.

During the past decades, a substantial effort has been made to increase the H_2 flux by decreasing the membrane thickness from about a millimeter to micrometers and even submicrometers.[6] However, the increase in flux by reducing the membrane thickness approaches its limits, as submicron membranes do have a high flux but show poor mechanical strength. The mechanical strength of the membrane can be increased by deposition of the membrane layer on a relatively thick porous support, but this will also induce an increase in the transport resistance for H_2. Although the specific resistance in the support is relatively low as compared to that of the membrane layer, the H_2 flux is limited significantly due to the thickness of the support. Additionally, mass transfer resistances in the gas phase at the feed and retentate side as well as in the porous support become more pronounced at a lower membrane thickness. Moreover, the interface between the Pd surface and the bulk can represent an additional resistance, either due to free energy differences between H atoms in the surface layer and the bulk or due to the dissociation of H_2 at the feed side or association of H atoms at the permeate side of the membrane.[7]

The reduction of the membrane thickness is not only limited by the mechanical strength but also by the formation of pinholes during fabrication. To prevent pinhole formation, it has been suggested that membranes with a thickness of at least 3 times the diameter of the pores in the top layer of the support need to be made.[8] Moreover, as it is well-known that ceramic porous supports are seldom defect free, this will also decrease the selectivity of the supported membranes.

This paper describes the application of microsystem technology to increase the hydrogen flux through Pd-based membranes and to prevent the formation of pinholes during membrane fabrication. For this purpose Pd and Pd/Ag alloy membranes have been produced. It will be shown that fluxes can be achieved that are substantially higher than the fluxes obtained with Pd layers deposited on porous supports.

Experimental Section

The permeability and selectivity of the membranes were determined in the experimental setup shown in Figure 1.[9] The retentate and permeate side were continuously flushed: the retentate side with a known mixture of H_2 and He and the permeate side with N_2. All gas flows were regulated by mass flow controllers. The retentate and permeate flow rates were varied between 100 and 1000 mL/min. The purity of H_2, He, and N_2 used was 99.999%. The absolute pressure of the retentate side was controlled by a pressure controller and was set slightly above atmospheric pressure. The transmembrane pressure was kept below 20 mbar. The permeability and selectivity were determined by measuring the H_2 and He concentration in the N_2 stream by a GC equipped with a thermal conductivity detector (TCD).

The membranes were activated for at least 3 h at a temperature of 673 or 723 K, respectively, depending on the operating temperature of the first experiment. During activation, a mixture of 20 vol % H_2 and 80 vol % He was fed to both the retentate and permeate side of the membrane. After activation, pure He was fed to

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† Eindhoven University of Technology.
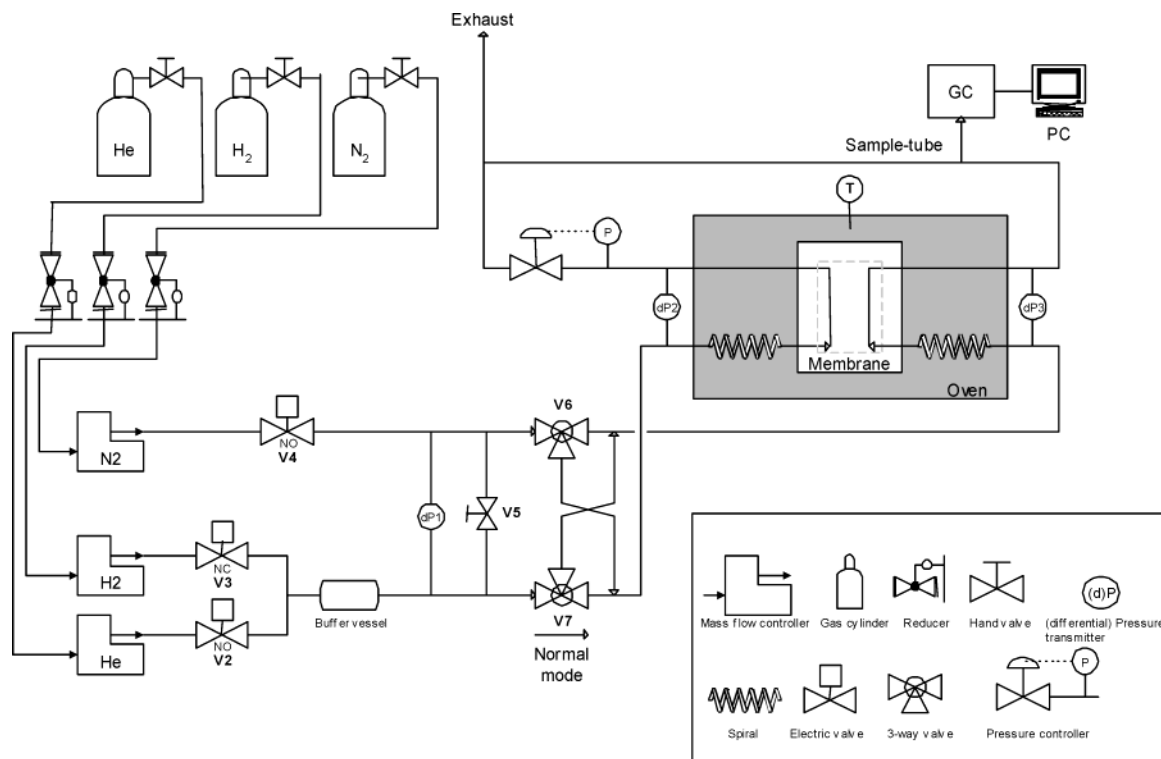
‡ University of Twente.

§ Aquamarijn Microfiltration BV.

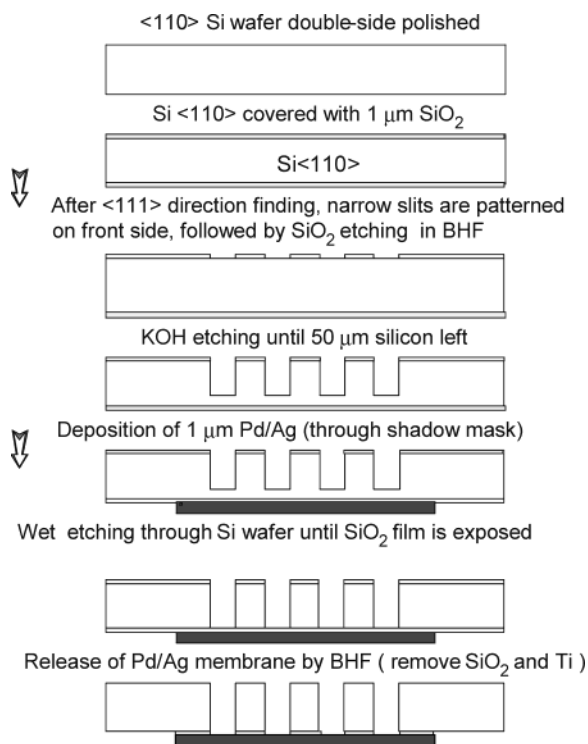**Figure 1.** Schematic representation of the setup used for permeation experiments.

Figure 2. Steps followed to manufacture a free-hanging membrane.

Figure 3. Two photographs of the free-hanging membrane: (a) top view of the aperture side and (b) SEM picture of the cross section perpendicular to the apertures.

Results and Discussion

Fabrication of Free-Hanging Membranes. For all membranes described in this paper, a double-side polished silicon substrate (wafer) with crystallographic cut ⟨110⟩ served as the basis. The substrates were 350 μm thick and 3 in. in diameter. The general procedure for the manufacturing of free-hanging membranes is summarized in Figure 2.[10,11] A 1 μm protective layer of wet, thermally oxidized SiO_2 was deposited on both sides of the wafer. After precise alignment to the ⟨111⟩ crystal direction, which is crucial for sharp and precise etching of structures with high aspect ratio, parallelogram-shaped structures of 25 × 1250 μm were imprinted on one of the SiO_2 layers by standard photolithography. The SiO_2 layer was removed at the

the retentate side and pure N_2 to the permeate side in order to detect any He leak through the membrane. During the leak test, a transmembrane pressure of 50 mbar was applied, and four samples were taken. Hydrogen permeation experiments were carried out at 623, 673, and 723 K, and the H_2 partial pressure in the feed was varied from 0 to 0.83 bar. The flux was measured only after the flux was stabilized, for which typically 24 h was required.
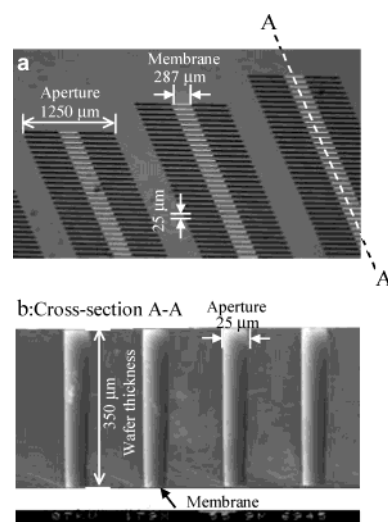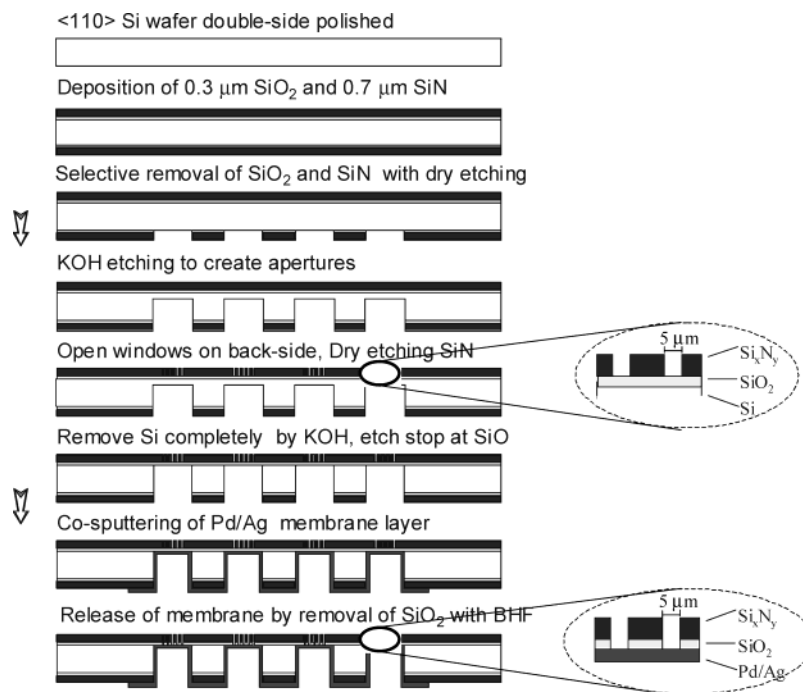
Figure 4. Steps followed to manufacture a microsieve-supported membrane.

imprints with buffered hydrofluoric acid (BHF) dry etching. When the SiO_2 protection layer was removed, apertures could be etched with KOH inside the wafer. The wet etching was stopped after the apertures reached a depth of 300 μm. A Si layer of 50 μm remained to give enough mechanical strength for the next step. Subsequently, the actual Pd or Pd/Ag membrane was deposited by (co)sputtering through a shadow mask on the other side of the wafer, using titanium (Ti) as an adhesion layer. The underground was still closed, which is a large advantage to prevent the formation of pinholes compared to depositing metal layers on top of a porous material. The thickness of the membranes was varied between 0.5 and 1.2 μm. After deposition of the metal layer, the remaining 50 μm of silicon is removed with KOH etching, followed by releasing the membrane layer by etching the SiO_2 and Ti layer with BHF. In Figure 3a, the top view of the aperture side is given; the white part in the middle of the aperture is the Pd or Pd/Ag membrane. In Figure 3b, a SEM photo is given of the cross section of the apertures.

Fabrication of Microsieve-Supported Membranes. The manufacturing of microsieve-supported membranes deviated in some steps from that of the unsupported membrane. The fabrication steps are given in Figure 4. First, a 0.3 μm protective layer of SiO_2 was deposited on both sides of the wafer, followed by a 0.7μm Si_xN_y layer. Parallelogram-shaped structures of 350 × 2100 μm were imprinted on the Si_xN_y layer on one of the sides of the wafer by standard photolithography. The longest side of the parallelogram was aligned to the $\langle 111 \rangle$ direction of the Si wafer. The Si_xN_y was removed at the imprints by dry etching (reactive ion etching, RIE). After the SiO_2 protection layer was removed, apertures could be etched with a KOH solution inside the wafer. The wet etching was stopped after the apertures reached a depth of 300 μm, again to give enough mechanical strength in the subsequent step.

At the microsieve side, a pattern of circular openings of 5 μm in diameter was imprinted on the Si_xN_y layer, followed by dry etching of the Si_xN_y layer. The SiO_2 layer
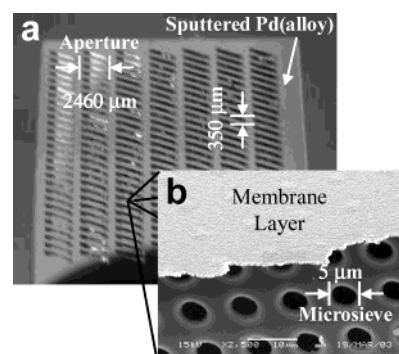

Figure 5. Two photographs of the microsieve-supported membrane: (a) top view of the aperture side and (b) SEM picture of the membrane layer deposited on top of the microsieve (membrane layer was partly removed to show the microsieve).

was left intact to provide a closed substrate in order to avoid the formation of pinholes during sputtering of a Pd/Ag layer inside the aperture at the SiO_2 layer of the microsieve in a later step. From the dimensions of the aperture it can be expected that the microsieve can withstand a pressure of at least 4 bar. In the next step, the remaining 50 μm of Si in the parallelogram-shaped apertures was removed by KOH etching, followed by sputtering of the membrane material onto a surface area of 18 × 18 mm at the aperture side (Figure 5a). Besides the bottom of the aperture (Figure 5b), later forming the actual membrane, also the sidewall of the aperture and the wafer area around the aperture were covered by the membrane material during sputtering. Here also, prior to the sputtering of membrane material, a Ti layer was sputtered to obtain a good adhesion between the SiO_2 and the membrane layer. In the final step, the SiO_2 and the Ti in the circular openings at the microsieve side were removed with BHF to release the membrane area at the microsieve side.

Metal Film Deposition. The purity of the Pd and Ag targets was 99.99 wt %. The Pd membrane was deposited by single cannon sputtering of a 1.0 μm Pd layer on top of the SiO_2 layer. The Pd/Ag alloy mem-
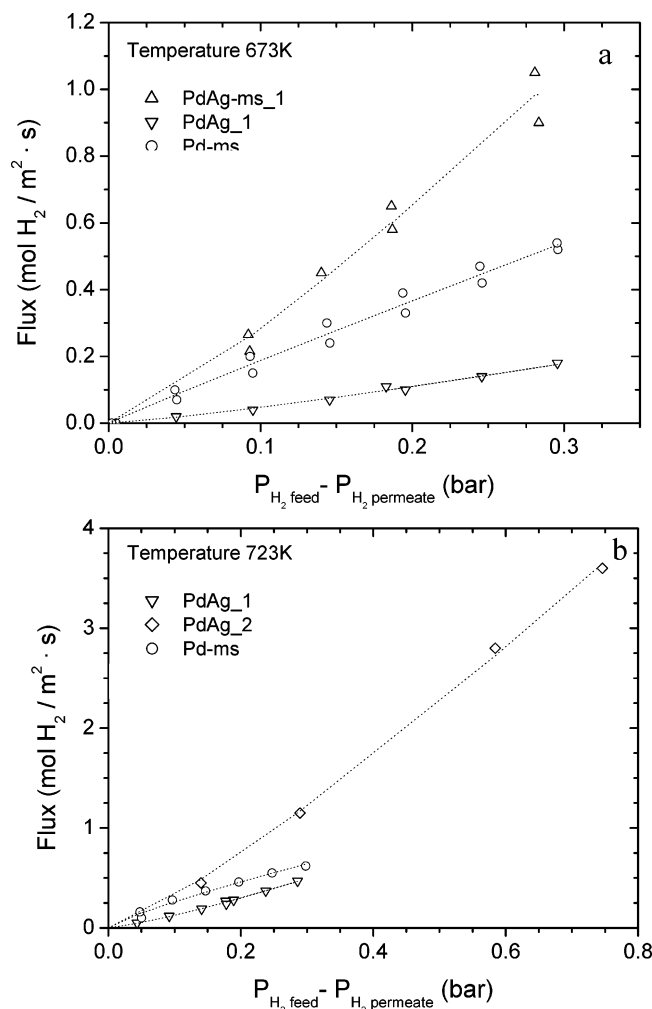
Figure 6. Hydrogen flux as function of the hydrogen partial pressure in the feed: (a) measurements at 673 K and (b) measurements at 723 K (lines are to guide the eye). PdAg_1 and PdAg_2 are free-hanging PdAg membranes of 1.2 and 0.7 μm thickness, respectively; PdAg-ms-1 and Pd-ms are microsieve-supported membranes of 0.7 and 1.0 μm, respectively.

brane was fabricated by using two ion cannons. The use of two separate ion cannons allows us to sputter Pd and Ag simultaneously with a homogeneous Pd/Ag composition as a result. By changing the operating conditions of the two sputter cannons, all possible alloy compositions can be obtained. The Pd/Ag ratio of the membrane was adjusted by using a previously obtained relation between sputtering parameters and final Pd and Ag concentrations. However, only two compositions were made: 77/23 wt % Pd/Ag and 78/22 wt % Pd/Ag. During sputtering, the power supplies for the Pd and Ag targets were 135 and 26 W, respectively, at a pressure below 1 Pa and at a temperature of 673 K. The thickness of the Pd/Ag membranes was varied between 0.5 and 1.2 μm.

Permeability and Selectivity Measurements. During the permeation measurements, He could not be detected in the permeate for both the pure Pd and Pd/Ag alloy membrane, so the selectivity of the membranes is in excess of 1500. Also based on single gas permeation experiments, it could be concluded that the membranes are pinhole free. The results of experiments with varying H_2 concentration in the feed are given in parts a and b of Figure 6 at 673 and 723 K, respectively. The measured flux is plotted against the difference in H_2 partial pressure of the feed inlet and the permeate
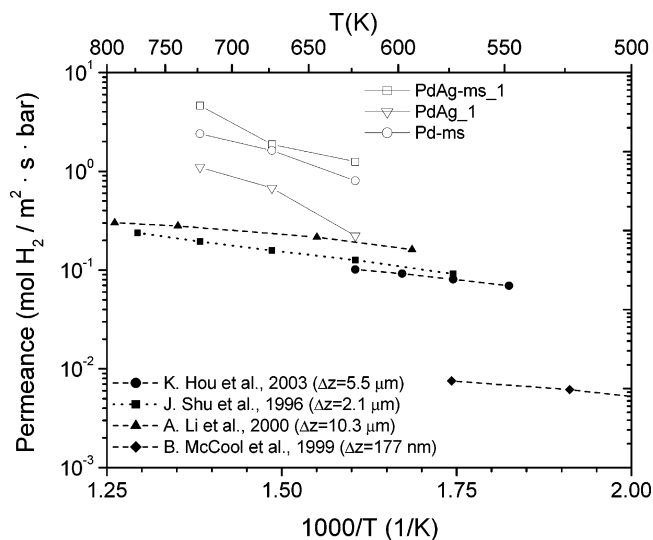

Figure 7. Comparison of membrane permeances presented in this work with hydrogen selective membranes deposited on a porous substrate.

outlet. From these results it follows that the measured H_2 flux through the membrane can be described by

$$F_{H_2} = P(T)(P_{H_2\text{ret}}{}^n - P_{H_2\text{perm}}{}^n) \qquad (1)$$

in which F_{H_2} is the H_2 flux; $P(T)$ is the permeance; and $P_{H_2\text{ret}}$ and $P_{H_2\text{perm}}$ are the H_2 partial pressure at the retentate and permeate side, respectively. The value of the exponent n depends on the transport step that limits the hydrogen flux. If only diffusion through the membrane limits the flux, n will be equal to 0.5 (also known as Sievert's law). If surface reactions limit the flux, n will be unity, and when both transport steps limit the flux, n will vary between 0.5 and 1.0. To determine which step limits the H_2 transport rate, the measurements with varying H_2 feed concentrations have been fitted to eq 1 to obtain the value of n. In the case of the Pd membrane, the H_2 permeation is partly limited by the diffusion through the membrane at 723 K (n is around 0.9), and at 673 K the influence of diffusion is hardly noticeable (n is close to 1). In the case of the Pd/Ag alloy membranes, a value larger than 1 has been found for n. A possible explanation for this phenomenon could be surface segregation,[12,13] leading to enrichment of silver in the surface layer. As this enrichment process is rather slow, it also explains the long stabilization times after a change in feed composition. Additionally, the adsorption of gases at the metal surface can influence the degree of segregation.[14] The presence of hydrogen will repress the preference of Ag for a location at the surface. Because more Pd will be present at the surface at increasing H_2 partial pressure, more active sites will be available for the necessary surface reactions to adsorb and desorb H_2 from Pd. As a result, the dependency of the flux upon the H_2 partial pressure can be larger than proportional ($n > 1$).

In Figure 7 the permeances of the membranes fabricated with microsystem technology are compared to Pd and Pd/Ag alloy membranes deposited on porous substrates. All permeances are calculated on the basis of n = 1. The microsystem-fabricated membranes give the highest permeances, even up to a factor 10 higher than for membranes deposited on porous substrates. In principle, large increments in permeance are still pos-

sible for the microsystem membranes if the limitation in H_2 permeation is changed from surface reactions to diffusion. Thin layers of 200 nm or less are possible,[19] which will allow for a further increase of the flux by a factor of 4. For the microsystem technology based membranes, the flux limitations due to mass transfer resistances in the gas phase will not be an issue because of the small dimensions of the gas ducts, especially if the flow can be forced through the slits.

Conclusions

In this paper we have shown that microsystem technology provides a powerful tool to come to high-flux Pd and Pd/Ag membranes that are pinhole free. These membranes exhibit fluxes that are about a factor of 10 higher than the fluxes obtained with Pd and Pd/Ag deposited on porous supports. We expect that these fluxes can still be improved significantly, thus opening the way for large-scale application.

Acknowledgment

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