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Stability investigation of micro-configured Pd–Ag membrane modules – Effect of operating temperature and pressure

T.A. Peters*, M. Stange, M.F. Sunding, R. Bredesen

SINTEF Materials and Chemistry, P.O. Box 124 Blindern, N-0314, Oslo, Norway

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ABSTRACT

The long-term stability over a period of up to 50 days has been reported for various designs of microstructured $Pd_{77}Ag_{23}$ membrane modules for H_2 production and purification. Even though microchannels provide sufficient mechanical support for moderate trans-membrane pressure difference and temperatures, *i.e.*, 4–5 bars and 400–450 °C, long-term operation under these operating conditions results in a large deformative settling of the $Pd_{77}Ag_{23}$ film into the microchannel support. This settling leads to microstructural changes and pore formation on the feed surface of the membrane film that ultimately results in membrane failure. For pressures above approximately 5 bars, the application of microchannel-supported modules is thus not feasible, and for that purpose a continuous porous stainless steel support is introduced that allows for a sufficient stabilisation of the thin $Pd_{77}Ag_{23}$ films. For such a porous stainless steel supported microchannel module, a hydrogen flux of 195.3 mL cm^{-2} min^{-1} is obtained at 450 °C and 5 bars feed pressure, corresponding to a permeability of $3.4 \cdot 10^{-8}$ mol m^{-1} s^{-1} $Pa^{-0.5}$. During the complete operation of 1100 h at 450 °C, the module shows a very good stability up to the highest feed pressure applied of 15 bars. The N_2 leakage flux has remained below the detection limit of the equipment, 5 μL cm^{-2} min^{-1}, resulting in a minimum value for the H_2/N_2 permselectivity of 39.000 applying the pure H_2 flux value obtained at 5 bars.

Introduction

Palladium (Pd) and many Pd-alloys have high solubility and diffusivity of hydrogen, and are therefore promising as membranes for medium to high temperature hydrogen separation (250–550 °C) [1,2]. Compared to other types of hydrogen separation membranes [2], Pd-based membranes provide the best hydrogen flux-selectivity combination, and possible applications are typically found in hydrogen production, recovery and purification [1,3–8], hydrogenation [9] and dehydrogenation [9,10] processes. Current membrane technology comprises self-supported and mechanically supported composited structures. Self-supported membranes are usually tubes or foils with thickness range of 50–100 μm with thicker membranes used at higher total trans-membrane pressure [11]. To reduce cost and increase flux, composite membranes consisting of membranes of 2–10 μm thickness

* *Corresponding author.*
E-mail address: thijs.peters@sintef.no (T.A. Peters).
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deposited on porous steel or ceramics are being developed [1]. Composite membranes have successfully been operated at laboratory scale and small pilot scale producing hydrogen for up to 13.000 h [12], and the technology appears ready for up-scaling. However, operation of these high-performing Pd-based membranes has made external mass transfer limitations, or concentration polarization, due to depletion of H_2 in the gas-phase layer next to the membrane surface critically important for some module designs and operating conditions [13–15]. This reduces the efficient partial pressure of hydrogen, and thereby also the pressure gradient sustaining the hydrogen flux. For example, the obtained H_2 flux in the world's largest scale membrane reformer equals only 50% of the flux value assuming bulk diffusion of hydrogen through the Pd membrane as rate determining step [16,17]. The main cause of the flux reduction is believed to be concentration polarization [13,18].

These gas phase limitations can only be reduced by smart membrane and module design in order to optimize feed flow conditions to reduce the thickness of the hydrogen-depleted layer. Microstructured membrane reactors that reduce gas phase diffusion limitations and increase the membrane area to reactor volume ratio compared to traditional tubular reactors, offer in this respect great advantages. Since concentration polarization effects are expected to be subordinate, a high space–time-yield is anticipated due to the supplied high volumetric surface area for reaction and membrane separation.

We have previously reported on the integration of thin unsupported Pd–Ag films in microchannel-configured devices that drastically reduce the distance between the bulk of the feed gas and the Pd membrane surface to the sub-millimetre region thereby reducing concentration polarization effects. For example, membrane modules have been fabricated where the thin Pd–Ag films are simply clamped between polished microchannel-configured flanges. For moderate trans-membrane pressure difference, *i.e.*, up to 1–3 bars, and for temperatures not higher than 400 °C, microchannels with a width between 200 μm and 1000 μm provided sufficient mechanical support even for the thinnest membranes tested, down to 1.4 μm [19]. Moreover, mixed gas permeation experiments revealed that concentration polarization effects are expected to be subordinate [20]. Along the same line, all-metallic membrane modules with micro-machined plates directly attached to the membrane by laser welding have been fabricated by the Karlsruhe Institute of Technology (KIT) applying the SINTEF thin free-standing films [20]. This is considered to be a very practical approach, and represents a first step towards a compact multi-layered microchannel membrane reformer system. In this work, membrane stability was achieved up to at least 4.5 and 3 bars for 13 and 4.7 micron thick $Pd_{77}Ag_{23}$ membranes, respectively [20]. The maximum bursting pressure was never reached during the experiments showing that the microchannels serve as a good support for the palladium membranes. The long-term stability for these microchannel membrane modules, however, has not been reported to our knowledge.

In the present work, we report a more thorough investigation of the long-term stability of various designs of microstructured membrane modules. In all modules, a microchannel-configured feed section is applied consisting either of 200 or 1000 micron-wide channels. On the permeate side, a stainless steel plate with apertures corresponding to the channel geometry, or a porous stainless steel (PSS) for application at higher feed pressures is applied. In the experiments, the H_2 permeation performance and stability of the modules are verified over a period of up to 50 days, while systematically increasing both temperature and pressure. Tested microstructured membrane modules are characterised employing different techniques, including scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and white light interferometry (WLI).

Experimental

Experimental

$Pd_{77}Ag_{23}$ films were prepared using a CVC 601 magnetron sputtering apparatus. The membranes were sputtered from a $Pd_{77}Ag_{23}$ target onto silicon single crystal substrates. The vacuum chamber was pumped down before introducing the sputtering gas Ar (99.9999%) into the system. Membrane films with a nominal thickness of 10 micron were applied in the current work.

Film integration in various membrane module configurations

After sputtering and removal from the silicon wafer, the free-standing $Pd_{77}Ag_{23}$ film has been integrated in various membrane module configurations. The membrane growth side from the sputtering process was always placed facing the feed housing of the apparatus, while the side that faced the substrate always faced the permeate side.

A stainless steel plate with apertures corresponding to the channel geometry, or alternatively, porous stainless supports, can be employed for mechanical support. In all microchannel modules employed in this study, a microchannel-configured feed section has been applied consisting either of 200 or 1000 micron-wide and deep channels. The 200 micron-wide micro-channel system consisted of fifteen channels machined with dimensions 0.2 × 0.2 × 13 mm, providing for a 0.39 cm^2 active membrane area. In addition, the circular gas inlet and outlet areas with a diameter of 500 μm provided an area of 0.059 cm^2, giving a total effective area for permeation of 0.449 cm^2. The 1000 micron-wide micro-channel system consisted of seven parallel channels machined with dimensions 1 × 1 × 13 mm^3, providing in total for a 0.91 cm^2 active membrane area. This area was applied in the calculation of flux, permeance and permeability. On the permeate side, a stainless steel plate with apertures corresponding to the channel geometry, or a porous stainless steel for application pressures above 5 bars have been applied (SIKA-R1, 1 micron rating supplied GKN Sinter Metals, Germany). The thickness of the porous support was 3 mm, while the employed microchannel-configured support plate had a thickness of 1 mm. More information on the applied modules can be found here [15,19,20].