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Performance and application of thin Pd-alloy hydrogen separation membranes in different configurations

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ABSTRACT

In the present article, constrains in performance, operating conditions and applicability of various Pd membrane configurations are discussed. The results demonstrate the high flexibility and versatility of the thin Pd-based membranes prepared by the two-stage fabrication method developed by SINTEF. The opportunity to apply the same membrane in different configurations enables assessment and investigation ranging from the basic membrane properties, effects of membrane design and composition, to identification of optimum working conditions in different applications. A noticeable result coming out of this study is the strong effect of concentration polarisation, and the possibility to limit this effect using the microchannel configuration.

1. Introduction

Hydrogen is used in many industry sectors and is one of the most important chemical commodities. It can be produced in several ways from water, hydrocarbons, alcohols and carbohydrates. Palladium has a high hydrogen solubility, hydrogen permeability and hydrogen selectivity, and is thus a suitable material for hydrogen separation membranes. Some areas where Pd-alloy membranes for hydrogen separation and purification have technological relevance include hydrogen production as fuel for fuel cells and combustion, for hydrogenation/dehydrogenation processes in the (petro)chemical industry, and hydrogen recovery and purification in various processes.

The main drawback of these membranes so far has been the high cost of the membrane material, which is strongly linked to the thickness (15–20 μm) of current commercial membranes. For broad use, it is therefore necessary to develop membranes with a reduced thickness of the Pd layer. In the last decade, a substantial research effort has been carried out to achieve higher fluxes by depositing thin layers of Pd or Pd alloys on porous supports, like ceramics or stainless steel. The most common methods to fabricate these composite membranes include electroless plating (Hou and Hughes, 2003; Keuler *et al.*, 1999), chemical vapour deposition (Itoh *et al.*, 2005; Xomeritakis and Lin, 1996), physical vapour deposition (Basile *et al.*, 1996), and sputtering (Jayaraman and Lin, 1995; Jayaraman *et al.*, 1995; McCool *et al.*, 1999; O'Brien *et al.*, 2001). In most cases, the thin Pd or Pd-alloy layer is prepared directly on the surface or inside the pores of the support (Tong *et al.*, 2005; Xomeritakis and Lin, 1996). Depending on the method, a lower thickness limit exists for which a dense layer can be obtained (Bredesen *et al.*, 2004). This thickness limit increases with increasing roughness and pore size in the support top layer (Jayaraman and Lin, 1995; Mardilovich *et al.*, 2002). A layer-to-pore size ratio, LP = (separation layer thickness)/(support layer pore diameter) (m/m), may be defined, and this is typically of the order 100 or higher (Bredesen *et al.*, 2004). In general, a low LP is advantageous for high rate hydrogen permeation.

SINTEF has developed membranes of 1–5 μm thickness giving an increased cost-performance benefit, both due to the lower materials cost and the significantly higher flux obtained. Different from previous efforts we apply a two step process where the defect free Pd-alloy film is first prepared by sputtering deposition onto the extremely smooth surface of a silicon wafer (Bredesen and Klette, 2000; Peters *et al.*, 2008). In a second step the film is removed from the wafer allowing the preparation of very thin membranes. These films may subsequently either be used self-supported or integrated with various supports of different pore size, geometry and size. Moreover, the magnetron sputtering technique allows for the

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preparation of very homogeneous films of controlled thickness from multi-component targets, this in contrast to the more commonly applied electroless plating method where thickness and composition control is more cumbersome (McCool *et al.*, 1999).

The flexible manufacturing method opens for applications ranging from micro-electromechanical system (MEMS) integration to large-scale power plants with CO_2 capture. In this presentation, three types of membrane configurations, self-supported (LP → 0), microchannel-supported (LP = ∼0.001), and tubular-supported (LP = ∼1), are described. The different configurations are sketched in Fig. 1. Typical performance, operating conditions and applicability of the various configurations will be discussed. Moreover, implications of the chosen configuration on concentration polarisation effects, that is gas phase diffusion limitations in the direction perpendicular to the membrane surface, are discussed. The configurations studied are relevant for applications from mm^2 to km^2 range, and operation conditions employing differential pressures ranging between ∼0 and ∼3 MPa.

The various configurations provide different opportunities, both scientifically speaking and for practical use. The self-supported configuration allows studies of membrane properties without the influence of any porous support structure, though only low total pressure differences can be applied. The typical disk-shaped or rectangular geometry of the steel frames fixing the membrane in-between (Fig. 1(a)) has the disadvantage of giving a somewhat undefined gas flow pattern. The gas flow pattern is more defined in the microchannel configuration (Fig. 1(b)), enabling easier modelling and interpretation of flux data from gas mixtures. In addition, the strength of the thin membranes allows higher total differential pressures compared to the self-supported membranes. Thus, studies can be performed over a larger partial pressure range, and furthermore, without the use of a sweep gas on the permeate side. The latter point is important in defining the partial pressure of hydrogen at the permeate membrane surface. In the tubular configuration (Fig. 1(c)), experiments with even higher-pressure difference, and thus higher hydrogen flux, can be performed. Furthermore, using supports with a comparable pore size dimension as the membrane thickness give a negligible support resistance. The tubular configuration is commonly used in traditional liquid filtration, and appears as a preferred choice by membrane producers and end-users. The flow pattern is well defined, though upscaling to larger multi-tube modules typically not scales linearly for area versus flux.

2. Experimental

2.1. Pd-23%Ag film preparation

Palladium films were prepared by sputtering using a CVC 601 magnetron sputtering apparatus. The films were sputtered from a Pd-23%Ag target (FHR Anlagenbau GmbH, Germany) onto polished silicon single crystal substrates (Si-Mat, Germany). The vacuum chamber was pumped down to $\sim 10^{-6}$ Torr before introducing the sputtering gas Ar into the system. The final membrane thickness depends on the duration of sputtering, and was determined by a white light interferometer (WYKO NT-2000, Veeco Instruments).

2.2. Membrane preparation

After sputtering, the palladium film was removed manually from the silicon substrate and either used unsupported, integrated in a microchannel configuration, or rolled on a porous support. The free-standing membranes were mounted between two stainless steel plates with a circular opening of 2.4 cm^2 area, which corresponds to the active membrane surface area during the permeation measurements. The plates with the fixed membrane were placed in a stainless steel housing connected to the gas system. An image is shown in Fig. 2(a). Membrane thickness applied was ∼2.2 μm. One membrane was heat treated in air to obtain higher permeability, as previously described (Mejdell *et al.*, 2008). The microchannel system consisted of a stainless steel feed channel plate with six parallel channels machined with dimensions 1 mm × 1 mm × 13 mm. The inlet and outlet tubes distributed and collected the feed and retentate gas, respectively. The Pd-23%Ag membrane was placed between the channel housing and a stainless steel plate with apertures corresponding to the channel geometry. Images are shown in Fig. 2(b). The stainless steel plate was employed for mechanical support. In total, the six channels provided for a 0.78 cm^2 active membrane area. On the permeate side an open housing was employed below the stainless steel plate. The membrane thickness was ∼1.4 μm, and more information can be found in (Mejdell *et al.*, 2009). Tubular-supported membranes were prepared by transferring the Pd-alloy film onto tubular macroporous stainless steel substrates (Bredesen and Klette, 2000). The tubular porous 316 L stainless steel (PSS®) Accusep™ support was supplied by Pall Corporation, USA. It has an average pore size of 2 μm. The diameter and wall thickness of the support were 11.85 and 0.48 mm, respectively. The effective surface area of the membrane was ∼6.8 cm^2, and the membrane thickness was ∼2.2 μm. Further information on the preparation of the tubular-supported membranes could be obtained from (Peters *et al.*, 2008). The tubular-supported palladium membranes were tested in a unit designed and constructed for high-pressure membrane permeability testing. The supported palladium membrane was placed inside a 316 L stainless steel module (inside diameter 1.9 cm). An image of tubular-supported membranes is shown in Fig. 2(c).

2.3. Hydrogen permeation measurements

The membranes were ramped to the target temperature in an inert atmosphere of N_2/Ar, before H_2 was introduced, and the different testing conditions are summarized in Table 1. The feed and permeate gas flows were controlled by automated mass flow controllers (Bronkhorst High-Tech). The hydrogen flux through the membrane was determined by a film flow meter (HORIBA group, model SF-2) during experiments with the flat and microchannel

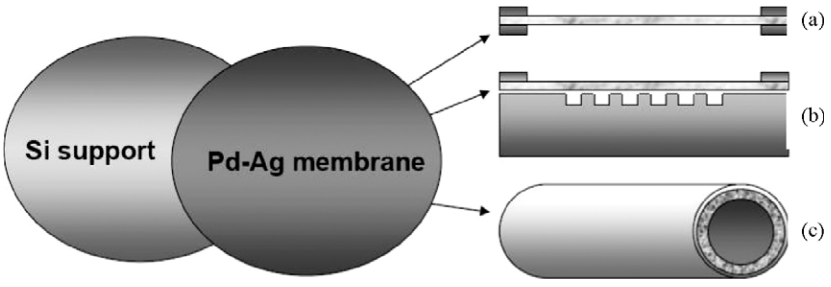

Fig. 1. The different assemblies presented: (a) self-supported; (b) microchannel configuration; (c) tubular-supported.