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Influence of the gas phase resistance on hydrogen flux through thin palladium–silver membranes

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ABSTRACT

Pure and mixed gas permeation tests were performed on Pd-based hydrogen selective membranes at different experimental conditions. In particular the permeance of pure hydrogen as well as of binary and ternary mixtures containing hydrogen, nitrogen and methane was measured, at temperatures ranging from 673 to 773 K and at pressure differences up to 6 bar. The membranes, supplied by NGK Insulators Ltd., Japan, were formed by a selective Pd–Ag layer (20 wt% Ag) deposited on a tubular ceramic support, and showed very high hydrogen permeance and a practically infinite selectivity toward hydrogen. Interestingly, the permeance values measured in pure gas experiments resulted always higher than those obtained in permeation tests with gas mixtures; in the latter case, moreover, the permeate flux significantly deviates from Sieverts' law based on the hydrogen partial pressure in the bulk gas phase. Both facts suggest the existence of non-negligible resistances to hydrogen transport in the gas phase itself, in addition to that offered by the metallic membrane. Experiments performed with increasing feed flow rates, showed also an increase in hydrogen permeance thus revealing the importance of the concentration polarization effects inside the module. Gas phase mass transport coefficients were calculated and used to determine the role of such a resistance in the overall mass transport process. The Sherwood number was also evaluated and was found to follow a boundary layer type of correlation. A general sensitivity analysis was performed in order to compare the effects on the transmembrane hydrogen flux of the two resistances, with different physical dimensions, offered by the gas phase and the metallic membrane. The concentration polarization number thus introduced allows for an *a priori* identification of the leading resistance at any operating conditions and gives clear indications on the actions required to improve the module performance.

1. Introduction

The use of hydrogen as a clean energy carrier has stimulated significant research efforts aimed at the production of gas streams with high purity. Most of the hydrogen is still produced by chemical reforming of natural gas, with a reaction widely used to produce synthesis gas for various chemicals [1], even though hydrogen could be derived from other sources using also different forms of power generation [2]. One of the most promising applications for hydrogen is in fuel cells, which are considered as an alternative power source in many fields thanks to the high efficiency shown with respect to normal combustion engines. On the other hand fuel cells need a highly pure hydrogen to avoid poisoning [3,4] and require optimal separation from various impurities such as N_2, CO_2, H_2O, CH_4, and, above all, CO contained in the steam reforming products. Palladium and palladium-based membranes are very promising tools for hydrogen purification due to their excellent physical and transport properties [5], which make the alloy permeable to hydrogen while remaining completely impermeable to other gases. Palladium-based membranes, providing a high permeate flux and ultra-pure hydrogen, can be produced nowadays, even though several different aspects are still open to questions [6,7], including membrane cost and lifetime. Presently the research focus is also evolving from mere membrane production and characterization to studies of membrane behaviour inside the separation modules or membrane reactors, in order to have valuable information for the development of pilot scale processes and for the system scale up. Indeed the peculiar characteristics of these membranes, with high rates of hydrogen permeation, can lead to accumulation of non-permeable gases and a depletion of hydrogen in the boundary layer close to the membrane [8–10]; concentration polarization phenomena, therefore, need to be taken into account for a proper modelling of the membrane apparatus and of the whole separation process. On the other hand, concentration polarization is very frequent in all membrane separation systems, even if it has not been extensively studied yet for palladium-based membranes.

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This work is focused on the analysis of such phenomena considering the hydrogen permeation behaviour of highly permeable and highly selective $Pd_{80}Ag_{20}$ membranes, in a wide range of operative conditions; different mixture compositions as well as different feed flow rates and temperatures are considered in order to monitor the presence of concentration polarization in the membrane module and to inspect its influence on the membrane efficiency as a function of the different operating parameters. The results show that the operating conditions experimentally applied span from the case in which the process kinetics is practically determined by membrane permeability, to the case in which concentration polarization offers the controlling resistance.

The analysis performed presents also a proper procedure to compare correctly resistances which have different physical dimensions; its application leads to the introduction of the dimensionless concentration polarization number, based on which one can estimate the relative importance of Sieverts' permeance and gas phase transport resistance at any given operating conditions.

2. Experimental: materials and equipment

The membranes used in the present work were provided by NGK Insulators Ltd. and consist of a dense Pd–Ag layer deposited on the external surface of a tubular asymmetric α-alumina support [11]. The selective coating was deposited in two separate steps: electroless deposition technique was first used to cover the ceramic top layer with a Pd coating which was then plated with a silver layer. The alloying of the two deposited metal layers was performed by the producer, via coating diffusion at high annealing temperatures.

The final metallic membranes, whose main characteristics are reported in Table 1, have a 2.5 μm thickness with silver content of about 20% by weight, an external diameter of about 1 cm and a total length of 9 cm. The membranes were received already sealed in one end with a stainless-steel plug, and endowed with a VCR fitting in the other end for easy coupling with the permeation module.

A schematic of the experimental set-up is shown in Fig. 1; the membrane was mounted in a custom-built stainless-steel shell-in-tube module, with an internal diameter of 55 mm and an available internal length of 175 mm, connected to the gas reservoirs through different pressure and flow controllers which enabled us to feed the module with mixtures of desired compositions and flow rates.

The different tubing leaving the module were also endowed with backwards pressure controllers and mass flowmeters on both permeate and retentate sides in order to maintain the desired pressure difference across the membrane and to measure the permeating flux. A gas chromatograph was connected to all the different streams of the system to obtain a direct on-line measurement of their compositions.

Table 1
Main characteristics of the membrane used in this work.

Membrane type	Blind membrane, external selective layer
Deposition technique	Electroless deposition in two separate steps
Membrane length	90 mm
Membrane outside diameter	10 mm
Support	Asymmetric α-Al_2O_3
Average pores diameter on top layer	100 nm
Metal thickness	2.5 μm
Silver–palladium composition	20 wt% Ag

The stainless-steel membrane module was located inside a tubular furnace to maintain the test temperature, and an additional heating element as well as a thermocouple were inserted close to the membrane for a more accurate temperature control. Further details on the experimental set-up are reported in a previous work [11].

The heating procedure was performed following a precise protocol, in agreement with the indications of the membranes producer; in particular the membranes were brought to the experimental temperature under nitrogen flow, at room pressure, and following a heating ramp of 100 K h^{-1}, in order to avoid the creation of thermal stresses on the selective coating. Before performing the first test in the newly received membranes, an air flow was maintained on the external side of the membrane for about 1 h, at the test temperature, in order to clean the surface and to optimize the membrane performance [12,13].

The membranes were tested at 673 ± 5, 723 ± 5 and 773 ± 5 K increasing the pressure in the shell side by subsequent steps and measuring the permeate flux and the composition of the different streams leaving the module. All the gases used in the experiments were gas-chromatographic grade with purity of 99.99% and were available at 11 bar; all tests were performed by using three different gases: hydrogen, nitrogen and methane. In particular, the experiments were performed by using pure H_2, pure N_2, H_2/N_2 mixtures (50 and 88 vol.% of H_2), H_2/CH_4 mixtures (50 vol.% of H_2) and the ternary mixtures $H_2/N_2/CH_4$ (50/25/25, vol.%). Tests were conducted at total differential pressures ranging between 0.2 and 6 bar, until constant steady-state values of permeate flux and composition were reached and the permeate, retentate and feed streams remained unchanged for at least 1 h.

For the different feed compositions, tests were performed by using three different feed flow rates, i.e. 1, 2 and 3 NL min^{-1}, and between tests the module was purged with nitrogen at a rate of

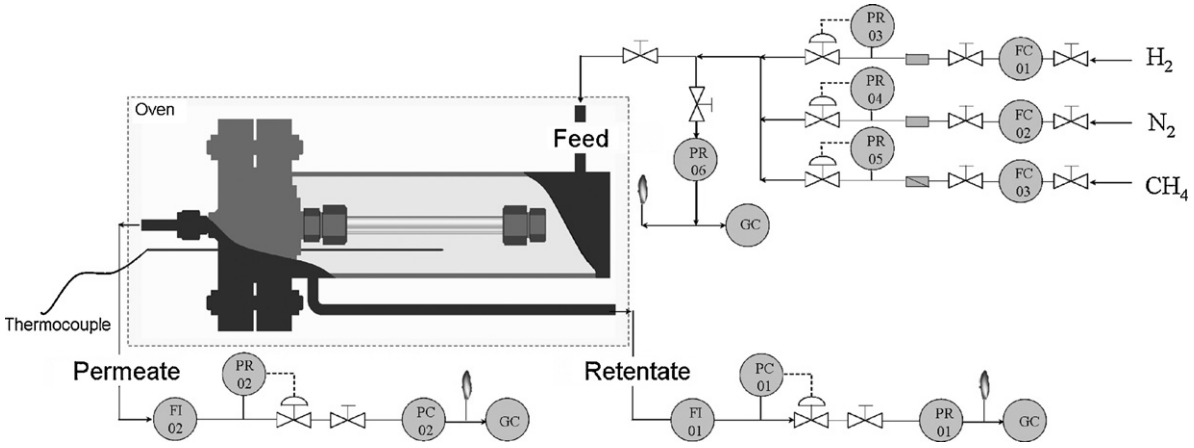

Fig. 1. Schematic of the custom-built, shell-and-tube apparatus used in this work.