Palladium based membranes and membrane reactors for hydrogen production and purification

**Citation for published version (APA):**

**DOI:**
10.1016/j.ijhydene.2017.03.067

**Document status and date:**
Published: 01/01/2017

**Document Version:**
Accepted manuscript including changes made at the peer-review stage

**Please check the document version of this publication:**
- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

**Link to publication**

**General rights**
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

**Take down policy**
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 16. Mar. 2020
Palladium based membranes and membrane reactors for hydrogen production and purification: an overview of research activities at Tecnalia and TU/e

E. Fernandez1,2*, A. Helmi2, J.A. Medrano2, K. Coenen2, A. Arratibel1,2, J. Melendez1,3, N.C.A. de Nooijer2, V. Spallina2, J.L. Viviente1, J. Zuñiga1, M. van Sint Annaland2, D.A. Pacheco Tanaka1, F. Gallucci2*

1 TECNALIA, Energy and Environment Division, Mikeletegi Pasealekua 2, 20009, San Sebastian-Donostia, Spain
2 Chemical Process Intensification, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5612 AZ Eindhoven, The Netherlands
3 Chemical Engineering and Environmental Department, University of the Basque Country UPV/EHU, C/Alameda Urquijo s/n, 48013 Bilbao, Spain

*Author to whom correspondence should be addressed: ekain.fernandez@tecnalia.com; f.gallucci@tue.nl

Abstract

In this paper, the main achievements of several European research projects on Pd based membranes and Pd membrane reactors for hydrogen production are reported. Pd-based membranes have received an increasing interest for separation and purification of hydrogen. In addition, the integration of such membranes in membrane reactors has been widely studied for enhancing the efficiency of several dehydrogenation reactions. The integration of reaction and separation in one multifunctional reactor allows obtaining higher conversion degrees, smaller reactor volumes and higher efficiencies compared with conventional systems. In the last decade, much thinner dense Pd-based membranes have been produced that can be used in membrane reactors. However, the thinner the membranes the higher the flux and the higher the effect of concentration polarization in packed bed membrane reactors. A reactor concept that can circumvent (or at least strongly reduce) concentration polarization is the fluidized bed membrane reactor configuration, which improves the heat transfer as well. Tecnalia and TU/e are involved in several European projects that are related to development of fluidized bed membrane reactors for hydrogen production using thin Pd-based (<5 µm) supported membranes for different application: In DEMCAMER project a water gas shift (WGS) membrane reactor was developed for high purity hydrogen production. ReforCELL aims at developing a high efficient heat and power micro-cogeneration system (m-CHP) using a methane reforming fluidized membrane reactor. The main objective of FERRET is the development of a flexible natural gas membrane reformer directly linked to the fuel processor of the micro-CHP system. FluidCELL aims the Proof-of-Concept of a m-CHP system for decentralized off-grid using a bioethanol reforming membrane reactor. BIONICO aims at applying membrane reactors for biogas conversion to hydrogen. The fluidized bed system allows operating at a virtually uniform temperature which is beneficial in terms of both membrane stability and durability and for the reaction selectivity and yield.

Keywords: Pd-membrane; Membrane reactor; hydrogen production; membrane manufacturing scale-up
1. Introduction

On an industrial scale, hydrogen is currently mainly produced by reforming of natural gas, an endothermic reaction system carried out at high temperature (> 850 °C) followed by high and low temperature water-gas-shift reactors and final hydrogen purification step(s) (see Figure 1) [1]. This conventional system is only efficient at very large scales, where heat integration can be optimized and the excess heat can be exported in the form of steam/power. The main problems for the reaction system are the thermodynamic constrains that limit both the steam methane reforming (endothermic) and water gas shift reactions (exothermic). To achieve high conversions and high hydrogen yields with high efficiencies, complex heat integration is required [2]. Until today, this process is still responsible of considerable greenhouse gas emissions since carbon dioxide capture actions are not implemented at industrial scale. Furthermore, the system cannot be easily scaled down and becomes rather inefficient at smaller scales. The efficiency of the process can be increased by exploiting process integration and process intensification. In this respect, integrating hydrogen production reactions and hydrogen recovery through membranes (named membrane reactors) results in shifting of the equilibria and thus higher efficiencies can be obtained. In ReforCELL project the steam and autothermal reforming (SMR/ATR) of methane was studied using membrane reactors. In FERRET the same reactions are being studied but using flexible natural gas as feed. In DEMCAMER project, a water gas shift (WGS) membrane reactor using Pd membranes was studied as an intensified process. When looking to remote installations, far away from natural gas grids and/or electrical grids, hydrogen can be produced from bio-renewable feedstocks. Among the various feedstocks, bioethanol is one of the preferred renewable sources for hydrogen production thanks to its unique features. Its hydrogen capacity is relatively high; it is easier to handle than hydrogen gas, being liquid and non-toxic; and even better, it is produced at global scale [3]. The bioethanol reforming using membrane reactors is being studied in FluidCELL project. Biogas is another renewable source for hydrogen production and it is produced during anaerobic digestion of organic substrates, such as manure, sewage sludge, the organic fractions of household and industry waste, and energy crops. It is produced in large scale digesters found preliminary in industrial countries, as well as in small scale digesters found worldwide. Biogas is also produced during anaerobic degradation in landfills and is then referred to as landfill gas. The European Biomass Organisation (AEBIOM) estimated a production of 39.5 Mtoe (≈48 bcm) in 2020, which corresponds to approximately 10% of EU natural gas consumption [4]. It must be outlined that the biogas production in the European Union has steadily increased over the last years. The biogas reforming membrane reactor is being evaluated in BIONICO project.

Figure 1. Conventional steam reforming reaction scheme. HT shift and LT shift are high and low temperature shift reactors respectively [1].
Pd-based membranes are mostly used for ultra-high H₂ purification due to their high H₂ permeances and selectivities compared to other materials. These membranes may be classified into unsupported and supported ones. Unsupported membranes are generally thick self-standing films (> 50 µm thick) in order to have a minimum mechanical stability. The main drawback of these membranes is their low hydrogen permeance associated to their bulk diffusion resistance. Moreover, as palladium is very expensive and since the permeation flux decreases with increasing the membrane thickness (i.e. more membrane area is required for the same hydrogen flow for thicker membranes) the costs of the membrane separation sharply increase by increasing the membrane thickness [5]. Thus, there is an optimum in membrane thickness related to the required membrane stability and permeance and costs of the membrane separation. For this reason it is foreseen that the first industrially available membranes will be supported membranes. Supported membranes consist of a thin selective film deposited onto a porous support that provides mechanical stability. However, in the total membrane cost, the cost of the support also becomes important, especially for very thin film membranes [6]. The selection of the support is of critical importance in the preparation of thin (< 5 μm) and defect-free palladium membranes. Asymmetric porous ceramic supports, having a gradual reduction in pore size from the bulk to the top layer, have a good surface quality to support very thin Pd-based membranes. However, they lack mechanical strength. On the other hand, metallic supports are more robust than ceramic ones, but the commercially available metallic supports, mainly tubular, have large and non-uniform pores and the surface has a rather low quality to be directly used as supports for very thin Pd membranes. In the case of membranes in which both the selective layer and the support are metallic and they are operated above the Tamman temperature (half the melting point), interdiffusion of both metals occurs, reducing the permeation performance of the membrane [7]. To solve this problem and to improve the quality of the surface, an inter-metallic diffusion barrier layer between the metallic support and the metallic selective layer is deposited.

Membrane reactors for methane steam reforming have been widely studied in the literature [8–10] for many different reactor configurations. The integration of dense Pd-alloy membranes in steam reformers leads to much higher conversion degrees compared to conventional systems and at much lower temperatures [11–15]. For small-scale hydrogen generation, especially for combined heat and power applications, the main advantage of membrane reforming resulting in a boost of efficiency, is the fact that high conversions can be achieved even at 600 °C [16]. Membrane reactors have been studied mostly considering a packed-bed reactor configuration [14,17]. However, the development of novel ultra-thin-film Pd-based supported membranes with extremely high H₂ permeances has arisen many drawbacks of this configuration, most of them are associated to bed-to-membrane mass transfer limitations, commonly referred to as concentration polarization [18,19]. Moreover, this configuration leads to large pressure drops, fact that can be circumvented by the use of bigger particles at the expense of increased intra-particle mass transfer limitations. Furthermore, temperature control in packed bed reactors may be problematic, especially for highly endothermic or exothermic reactions, with very limited freedom for different membrane and heat exchange arrangements [1]. All these drawbacks may be alleviated with fluidized bed membrane reactors [20]. While concentration polarization and temperature gradients can be largely reduced in fluidized beds, it has also been shown that stability issues related to attrition of the catalyst particles or erosion of the membrane surfaces may not pose major problems or can be overcome [21].

In the present work, the long-term stability of different type of thin Pd-based supported membranes is evaluated. In addition, the performance of fluidized bed membrane reactors for WGS and steam reforming of methane using these membranes is presented and it is compared with the performance of conventional reactors and fluidized bed membrane reactors using commercial thicker membranes. The main challenges to bring the Pd membranes closer to the market are also discussed.
2. Materials and methods

2.1 Membrane preparation: development and scale-up

Thin Pd-based supported membranes have been prepared onto ceramic and metallic porous supports for hydrogen purification and hydrogen production. Different membrane deposition techniques have been studied such as electroless plating (ELP), PVD-Magnetron Sputtering and combinations of those in order to obtain the best permeation properties for the membranes. Within DEMCAMER and ReforCELL projects, 3-5 µm thick Pd-Ag membranes supported on asymmetric porous alumina tubes (provided by Rauschert Kloster Veilsdorf) have been prepared by simultaneous electroless plating for WGS and steam methane reforming membrane reactors [22,23]. For their integration in reactors, these membranes have been connected to dense metallic tubes using a combination of Swagelok fittings and graphite ferrules [22,23]. Within ReforCELL project, 4-5 µm thick Pd-Ag membranes supported on porous Hastelloy X tubes (purchased from Mott Corporation) have been prepared by simultaneous electroless plating for steam methane reforming membrane reactor [24,25]. The metallic support was coated with Al₂O₃-YSZ prior to Pd-Ag membrane deposition to avoid intermetallic diffusion. In FluidCELL project ultra-thin Pd-Ag (~1 µm thick) membranes supported on porous alumina tubes have been developed by using two different approaches: (1) combination of PVD-Magnetron Sputtering and ELP [26] and (2) only by ELP [27]. In FERRET and BIONICO projects thin Pd-Ag-Au membranes with a gold content up to 10% wt. have been developed in order to enhance resistance to sulphur in natural gas and biogas reforming membrane reactors [28,29]. Figure 2 shows some of the Pd-based supported membranes mentioned above.

![Figure 2. Pd-based supported membranes developed in different projects: a) sealed ceramic supported thin Pd-Ag membrane (3-5 µm thick) [22], b) sealed ceramic supported ultra-thin Pd-Ag membrane (~1 µm thick), c) metallic supported thin Pd-Ag membrane [24,25], and d) ceramic supported Au coated thin Pd-Ag membrane (prior to annealing treatment) [28].](image)

From DEMCAMER project (started in 2011) to BIONICO project (started in 2015), Tecnalia has scaled-up the Pd membrane manufacturing process increasing both the number and length of membranes to be deliver for the prototype membrane reactors (see Table 1). In the beginning, 5-10 cm long Pd-based membranes were prepared and more recently 50 cm long membranes are being prepared for FluidCELL and BIONICO projects. Concerning the amount of membranes, in the first 4 listed projects 30-40 membranes were needed for the prototype, while for BIONICO project it is expected to integrate around 100 membranes in the prototype membrane reactor.

In DEMCAMER, ReforCELL and FERRET projects, two 20 cm long ceramic supported Pd-Ag membranes have been connected for their integration in the membrane reactor prototype (Figure 3a). The manufacturing of longer 50 cm long Pd membranes decreases the number of Swagelok-fittings...
for sealing (Figure 3b), reducing the cost of the sealed membranes as it is the case in FluidCELL and BIONICO projects.

Table 1. Number and length of Pd-based supported membranes manufactured for prototype membrane reactors.

<table>
<thead>
<tr>
<th>Project</th>
<th>Reference period</th>
<th>Number of membranes</th>
<th>Length of membranes after sealing (cm)</th>
<th>Prototype membrane reactor type</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEMCAMER</td>
<td>2011-2015</td>
<td>30</td>
<td>20</td>
<td>Packed bed WGS-MR</td>
</tr>
<tr>
<td>ReforCELL</td>
<td>2012-2015</td>
<td>30</td>
<td>20</td>
<td>Fluidized bed ATR/SMR-MR</td>
</tr>
<tr>
<td>FERRET</td>
<td>2014-2017</td>
<td>30</td>
<td>20</td>
<td>Fluidized bed natural gas reforming MR</td>
</tr>
<tr>
<td>FluidCELL</td>
<td>2014-2017</td>
<td>37</td>
<td>40</td>
<td>Fluidized bed bioethanol reforming MR</td>
</tr>
<tr>
<td>BIONICO</td>
<td>2015-2018</td>
<td>100</td>
<td>40</td>
<td>Fluidized bed biogas reforming MR</td>
</tr>
</tbody>
</table>

Figure 3. a) Two 20 cm long Pd-based membranes sealed together. b) 50 cm long thin Pd-based supported membranes.

2.2 Membrane permeation tests

2.2.1 Long-term stability test

The long-term permeation properties of the prepared membranes were characterized in a membrane permeation test equipment at TU/e. The tested membranes were: ceramic supported Pd-Ag membrane (4 µm thick), metallic supported Pd-Ag membrane (4-5 µm thick) and ultra-thin Pd-Ag membranes (~1 µm thick). The setup consists of three main sections: a feed section, a membrane module section and an analysis section [25,30]. At the feed section mass flow controllers from BROOKS b.v. were used to set the desired gas composition (e.g. N₂, H₂) and flow rate. The membrane module section consists of a stainless steel tube where the membrane is integrated from the top flange. The feed gas can be supplied to the module from the bottom part through a gas distributor (porous stainless steel plate with a pore size of 40 µm). Thus, the module can also be used for fluidization tests. The whole membrane module (reactor) is placed in an electric furnace to be able to set the desired temperature inside the reactor. Three temperature indicators were placed at different positions in the module to measure and monitor the temperature. A back-pressure regulator was placed at the outlet of the
module (retentate side) to set the required trans-membrane pressure difference (two pressure indicators were placed at permeate and the retentate side). Both retentate and permeate sections were connected to the analysis section (independently). The analysis section consists of mass flow meters (e.g from BROOKS, Bronkhorst) and film flow meters (from HORIBA) to measure the flow rate at the permeate side. At the retentate side a mass flow meter from BROOKS b.v. is placed. The outlet gases from both retentate and permeate sides can be analyzed with a µ-GC (CP-4900 series from Varian b.v.) or directed to the vent. For the tested membranes single gas test were performed feeding H₂ and N₂ independently. The hydrogen permeation flow rate was monitored with a Brooks mass flow meter and the N₂ leakage was measured using a Bronkhorst flowmeter (model F-110C-002; Nominal flow: 0.014 - 2 Nml/min air). Thus, the H₂ permeance and H₂/N₂ ideal perm-selectivity (ratio between H₂ and N₂ permeances) of the membranes have been determined over time. The obtained results for different membranes are presented in Section 3.1.1.

2.2.2 H₂S exposure test

In BIONICO project, the sulphur resistance of Pd-Ag and Pd-Ag-Au supported membranes has been evaluated [31]. Three membranes have been evaluated: Pd-Ag (E505), Pd-Ag-Au5% (E505) and Pd-Ag-Au7% (E506). Prior to each exposure the H₂ permeance of each membrane was measured by decreasing the pressure stepwise. After this measurement the membrane is exposed to a 2 l/min stream of H₂ and H₂S for 2.5 hours, followed by a permeance measurement under exposure of H₂S. This exposure allows to measure the inhibition effect at the different concentration of H₂S. During the regeneration cycle the temperature is increased up to 600 °C to desorb the sulfur with higher binding energies and increase the flux recovery [32]. After the recovery when a stable membrane flux was obtained the permeance is measured. The permeance during and after exposure are used to calculate the degree of inhibition and recovery compared to the initial permeance. In Table 2 the time and concentrations of the inhibition exposures are shown. All membranes followed similar exposure and recovery sequences, where the concentration of H₂S was sequentially increased. The tests results are presented in Section 3.1.2.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>1 ppm</th>
<th>3ppm</th>
<th>9ppm</th>
<th>17ppm</th>
<th>Total time of exposure [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdAg (E505)</td>
<td>X</td>
<td>X</td>
<td>X*</td>
<td></td>
<td>15.25</td>
</tr>
<tr>
<td>PdAgAu5% (E505)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>12.5</td>
</tr>
<tr>
<td>PdAgAu7% (E506)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>12.5</td>
</tr>
</tbody>
</table>

* At 9 ppm, H₂ flux was entirely inhibited so permeation test under H₂S exposure was suspended.

2.3 Membrane reactor tests

2.3.1 WGS membrane reactor

In DEMCAMER project, the performance of a fluidized bed WGS membrane reactor (FBMR) using five ceramic supported Pd-Ag membranes (4-5 µm) has been investigated and compared with the performance of a conventional fluidized bed reactor (FBR) [30]. The catalyst was 2 wt% Pt loading impregnated onto 80–200 µm size alumina particles. This catalyst and the alumina filler were supplied by Johnson Matthey. A fluidized bed membrane reactor setup with a H₂ production capacity
of 1 Nm$^3$/h H$_2$ was used including 5 sealed Pd-Ag supported membranes (total membrane area of \(~0.016$ m$^2$\)) (see Figure 4), more details on the setup are given in [30]. Table 3 illustrates the operating window in which the experiments were performed. In section 3.2.1, results from the experiments are plotted and discussed in terms of the main reactor performance characteristics, viz. CO conversion and H$_2$ recovery factor (moles of H$_2$ permeated through the membranes divided by total H$_2$ available inside the reactor). The process and flow diagram (PFD) of the setup used for the fluidized bed membrane reactor tests is shown in Figure 5. The setup consists of three main sections: a feed section, a membrane module section and an analysis section. The feed section consists of a feed gas supply from cylinders and mass flow controllers (Bronkhorst$^\text{®}$) to set the desired flow and feed composition at the inlet. A Bronkhorst$^\text{®}$ Controlled evaporator and mixer (CEM) system was used to feed the reactor with a precise and very stable amount of steam. All the lines were electrically traced to ensure that the temperature remains above the dew point of the gas mixture. The membrane module section consists of a stainless steel reactor (10 cm i.d. and 100 cm in height). Three electric ovens were used to keep the reactor at the desired temperature. Pressure transmitters (PTX 1400 from Druck Nederland B.V.) were used to measure the pressure at the top and bottom of the reactor (at the porous plate position). The analysis section consists of two inline GMS800 series extractive gas analyzers (© SICK GmbH). In the retentate side, the analyzer was calibrated for CO, CO$_2$, CH$_4$ and H$_2$ with a precision of 1 vol%. In the permeate side the analyzer was calibrated for H$_2$ between 0 to 100 volume % and for CO between zero and 100 ppm. Therefore, traces of CO impurity at the permeate side can be detected with the analyzer (with a lower detection limit of 0.2 ppm). CO$_2$ is also measured in the permeate side stream in the range 0–200 ppm. Figure 6 shows a conceptual drawing of the membrane reactor module including the temperature and pressure indicators.

Figure 4. a) Fluidized bed membrane reactor setup (capacity: 1 Nm$^3$/h H$_2$), b) 5 sealed Pd-Ag membranes ready for integration in the membrane reactor (~0.016 m$^2$ of membrane area).
Figure 5. PFD of the setup used for fluidized bed membrane reactor tests.

Figure 6. Details of the membrane reactor including temperature and pressure indicators.
Table 3. Overview of the operating window for the experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Tested conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (bar)</td>
<td>1–3</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>350–450</td>
</tr>
<tr>
<td>U/U_{mf} (-)</td>
<td>1.5–5</td>
</tr>
<tr>
<td>Steam/Carbon (-)</td>
<td>1.5–3</td>
</tr>
</tbody>
</table>

2.3.2. Steam methane reforming membrane reactor

In ReforCELL project, from one side, the performance of ceramic supported Pd-Ag membranes have been evaluated for steam and autothermal reforming (SMR/ATR) in a setup designed at TU/e. More details on the system are given in [23]. A Ru/Ce_{0.75}Zr_{0.25}O_{2} catalyst together with ZrO_{2} filler material (average sieved fraction of 260 μm, bulk density of 2100 – 2300 kg/μm), both provided by Hybrid Catalysis b.v., have been used in this study. The tests with autothermal reforming and steam reforming of methane have been carried out with different molar feed ratios of CH_{4}/H_{2}O/O_{2}/N_{2}. The volumetric flow rate was selected to ensure proper fluidization throughout the reactor (u/u_{mf} > 1.3). To reach the required total gas flow rate, the N_{2} flow rate has been increased slightly for experiments at higher pressures. Table 4 gives an overview of the used feed flow rates for the different experiments performed in the fluidized bed reactor setup. The experimental results were also compared to the results with commercial membranes from REB [33], where the flow rates were changed to maintain the same fluidization regime around the membranes (as the different membranes occupy a different cross-section of the reactor) (see results in Section 3.2.2).

Table 4. Experimental conditions for fluidized bed membrane reactor tests performed with REB commercial thick Pd-based membranes and ceramic supported Pd-Ag membranes from TECNALIA [23].

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Reaction</th>
<th>Membranes</th>
<th>ATR REB</th>
<th>SMR TECNALIA</th>
<th>ATR TECNALIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component feed flow rate (NL/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH_{4}</td>
<td>1.31</td>
<td>0.84</td>
<td>0.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N_{2}</td>
<td>4.78</td>
<td>7</td>
<td>6.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>2.69</td>
<td>0</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{2}O</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total flow rate</td>
<td>11.29</td>
<td>10.34</td>
<td>10.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed flow ratios</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen to Carbon Ratio (NCR)</td>
<td>5.30</td>
<td>8.33</td>
<td>8.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen to Carbon Ratio (OCR)</td>
<td>0.43</td>
<td>-</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam to Carbon Ratio (SCR)</td>
<td>1.92</td>
<td>2.98</td>
<td>2.98</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

On the other hand, the performance of metallic supported Pd-Ag membranes have been evaluated for steam and autothermal reforming (SMR/ATR). 300 grams of NiO/CaAl_{2}O_{4} catalyst provided by Johnson Matthey with a particle size ranging between 150 and 250 μm has been used in this case. Steam Methane Reforming (SMR) and Autothermal Reforming of Methane (ATR) were carried out in this system. For both cases a reference case with a steam-to-carbon ratio (S/C) of 3, a temperature of 500 °C, 4 bar absolute pressure inside the reactor and 10 % mole fraction of methane in the inlet
gas has been selected. For the case of ATR, some oxygen is added with the inlet gas in order to have an oxygen-to-carbon ratio (O/C) of 0.25. In all cases N₂ is used as internal standard for analyzing the carbon balance. The influence of different parameters has been studied for both reaction systems. All the details concerning the experiments performed in the reactor have been summarized in Table 5, and the results are presented in Section 3.2.2.

Table 5. Experimental conditions for tests performed in the fluidized bed reactor setup with metallic supported thin Pd-Ag membranes. The reference case is without membranes [25].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SMR Reference case</th>
<th>SMR Conditions tested</th>
<th>ATR Reference case</th>
<th>ATR Conditions tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>500</td>
<td>500-600</td>
<td>500</td>
<td>500-600</td>
</tr>
<tr>
<td>Inlet pressure (bar)</td>
<td>4</td>
<td>2-5</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Steam-to-carbon ratio (S/C)</td>
<td>3</td>
<td>2-4</td>
<td>3</td>
<td>2-4</td>
</tr>
<tr>
<td>Inlet flow rate (L/min)</td>
<td>4.4</td>
<td>3.5-5.2</td>
<td>4.4</td>
<td>3.5-5.2</td>
</tr>
<tr>
<td>CH₄ inlet composition (%v/v)</td>
<td>10</td>
<td>Not varied</td>
<td>Not varied</td>
<td>Not varied</td>
</tr>
<tr>
<td>Oxygen-to-carbon ratio (O/C)</td>
<td>0.25</td>
<td>Not varied</td>
<td>Not varied</td>
<td>Not varied</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Permeation results

3.1.1 Long-term stability test results

In DEMCAMER project, five Pd-Ag alloy membranes (4–5 µm thick) supported on porous alumina were integrated in a membrane module and the performance of the membrane module was investigated in the presence of the catalyst in the continuous bubbling fluidization regime at high temperature WGS conditions [30]. Figure 7 summarizes the long-term performance of the membrane module under the specified conditions. The membrane module showed a very stable performance during nearly 900 h of continuous operation in the bubbling fluidization regime at high temperature WGS conditions (including the initial time used for membrane activation), with a H₂ permeance of 4.2 x 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ and a H₂/N₂ ideal perm-selectivity of 10000-20000 at 400 °C and 1 bar of pressure difference.
In ReforCELL project, long-term stability tests at various temperatures (400-600 °C) of Pd-Ag (4-5 µm–thick) membranes supported onto metallic Hastelloy X porous supports (from Mott) have been performed (area per membrane: 4.3 x 10^{-3} m^2). Long term stability tests of two of these membranes is presented in Figure 8, where it is observed H\textsubscript{2} permeance and ideal selectivity for more than 800 h exposed to continuous permeation. In Figure 8 (left) ideal perm-selectivities above 200000 were reported at temperatures up to 600 °C with hydrogen permeances of about 1.3 x 10^{-6} mol m^{-2} s^{-1} Pa^{-1} [25]. At such conditions, after 800 h of tests N\textsubscript{2} leakages were observed leading to a decrease in selectivity to 2650, which is anyway relatively high as compared to literature data reported for metallic supported membranes. Further detailed characterization study is needed for understanding the behavior of Pd-based alloy supported membranes at high temperatures (>550 °C). The identification of the cause for the defect formation in the membrane (e.g. Ag sublimation, grain growth, sintering of the support, impurities during membrane preparation, etc.) will be crucial for developing novel long-term stable membranes for high temperature applications. On the other hand, the thickness of the ceramic layers should be increased in order to establish a stable barrier between a metallic support and the thin Pd-Ag alloy membrane layer at high temperatures. The H\textsubscript{2} permeation of the metallic supported Pd-based membranes is low compared to comparable ceramic supported ones, and in addition the cost of the metallic supports is much higher than the ceramic ones. Then the H\textsubscript{2} permeation should be increased and for that asymmetric porous metallic supports could be used. A second membrane (Figure 8 right) operated at 400 °C, thus less aggressive conditions, showed high stability with high perm-selectivities (>150000) [34].
Figure 8. H₂ permeance (open circles) and H₂/N₂ ideal perm-selectivity (closed circles) of two metallic supported thin Pd-Ag membrane as a function of time on stream at 500-600 °C (left) [25] and 400 °C (right) [34].

In FluidCELL project, a 1.3 µm thick membrane was tested for 1000 h at 400 °C and 1 bar pressure difference in order to assess its long-term performance [27,35]. The H₂ and N₂ flow rates were monitored over time in order to determine the evolution of the H₂ permeance and the H₂/N₂ ideal perm-selectivity as presented in Figure 9. The reactor was fed with air for two minutes to carry out the activation of the selective layer. After the activation, the membrane showed a H₂ permeance of 9.0-9.4 x 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹. Nitrogen suffered a small increase in its permeance too. During the first 400 hours, and after activation step, the H₂ permeance kept a constant value. After this period, another small increase in nitrogen was detected probably due to damaging of the membrane sealing. Afterward, the nitrogen permeation maintained constant until the end of the 1000 hours of operation with a constant H₂/N₂ ideal perm-selectivity of 1900.

Figure 9. H₂ and N₂ permeances and H₂/N₂ ideal perm-selectivity of the 1.3 µm thick membrane at 400 °C and 1 bar pressure difference over time [35].
In FluidCELL project, Pd-Ag membranes prepared by direct PVD-MS technique onto ceramic porous supports showed low H₂/N₂ selectivity (due to the very high N₂ permeance) but when depositing a thin Pd layer by ELP onto the PVD-MS layer the H₂/N₂ ideal perm-selectivity was 500 at 400 °C [26]. Moreover, the resulting composite layer (~1 micron thick) presented a very high H₂ permeance of 8 x 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ with a moderate H₂/N₂ ideal perm-selectivity of 500 at 400 °C and 100 kPa.

Table 6 compares the membrane permeation properties of the membrane prepared in this work with other Pd-based membranes reported in the literature. The membranes prepared in this work show similar or higher performance in some case compared with state-of-the-art membranes.

Table 6. Hydrogen permeation properties of thin Pd-based supported membranes prepared in this work and of other Pd-based membranes reported in the literature.

<table>
<thead>
<tr>
<th>Membrane Method</th>
<th>Thickness (μm)</th>
<th>H₂ permeance (10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹)*</th>
<th>H₂/N₂ ideal perm-selectivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-Ag/No support PVD 2 steps</td>
<td>1.9 – 3.8</td>
<td>190</td>
<td>2900</td>
<td>[36]</td>
</tr>
<tr>
<td>Pd-Au/Al₂O₃ ELP</td>
<td>2-3</td>
<td>62 (@ 500 °C)</td>
<td>1400 (@ 500 °C)</td>
<td>[37]</td>
</tr>
<tr>
<td>Pd-Au/YSZ-PSS ELP</td>
<td>1-5</td>
<td>43-52</td>
<td>10000-20000 (H₂/Ar)</td>
<td>[38]</td>
</tr>
<tr>
<td>Pd-Ag/α-Al₂O₃ ELP</td>
<td>2 to 10</td>
<td>6 – 31 (@ 350 °C)</td>
<td>500 to &gt;1,000 (@ 350 °C)</td>
<td>[39]</td>
</tr>
<tr>
<td>Pd/Metallic ELP</td>
<td>3 to 5</td>
<td>20 (@ 450 °C)</td>
<td>450 H₂/He (@ 450 °C)</td>
<td>[40]</td>
</tr>
<tr>
<td>Pd-Ru/Al₂O₃-PSS ELP</td>
<td>6.4</td>
<td>19</td>
<td>15000 @ 10 bar</td>
<td>[41]</td>
</tr>
<tr>
<td>Pd-Ag/α-Al₂O₃ ELP</td>
<td>3 to 9</td>
<td>15 (@ 350 °C)</td>
<td>&gt;7600 (@ 350 °C)</td>
<td>[42]</td>
</tr>
<tr>
<td>Pd/Metallic PVD+ELP</td>
<td>12</td>
<td>11 (@ 417 °C)</td>
<td>1,100 (@ 417 °C)</td>
<td>[43]</td>
</tr>
<tr>
<td>Pd-Ag/Al₂O₃ ELP</td>
<td>4</td>
<td>42</td>
<td>10,000-20,000</td>
<td>[30] this work</td>
</tr>
<tr>
<td>Pd-Ag/YSZ-Al₂O₃/Hastelloy X ELP</td>
<td>4-5</td>
<td>10</td>
<td>&gt;200,000</td>
<td>[24,25] this work</td>
</tr>
<tr>
<td>Pd-Ag/Al₂O₃ ELP</td>
<td>1.3</td>
<td>90-94</td>
<td>1900</td>
<td>[27] this work</td>
</tr>
<tr>
<td>Pd-Ag/ZrO₂ PVD + ELP</td>
<td>0.5 + 0.5</td>
<td>80</td>
<td>500</td>
<td>[26] this work</td>
</tr>
</tbody>
</table>

3.1.2 H₂S exposure test results

Three membranes have been evaluated: Pd-Ag (E505), Pd-Ag-Au5% (E505) and Pd-Ag-Au7% (E506) [31]. When exposing the Pd-Ag membrane to 1 ppm of H₂S at 550 °C, the H₂ permeance was the 38% of the initial H₂ permeance value (without H₂S content), while for Pd-Ag-Au 5% the H₂ permeance was the 51% of the initial value at the same H₂S content (see Table 7). The lower decrease in flux of the Pd-Ag-Au5% compared to the Pd-Ag membrane was expected due to the presence of gold, as previous reported by others [36]. This is also confirmed by Pd-Ag-Au7% membrane presenting a lower H₂ flux reduction (74% of the initial value) compared to Pd-Ag 5% and Pd-Ag membrane. The H₂/N₂ ideal perm-selectivity of the membranes was measured after the last H₂S
exposure and not during the experiment. The Pd-Ag membrane presented a perm-selectivity of 18 after 9 ppm H₂S and 15.25 hours of exposure. The selectivity values obtained for the Pd-Ag-Au5% and Pd-Ag-Au7% are respectively 793 after 9 ppm and 12.5 hours and 121 after 17 ppm and 12.5 hours. This shows that the decrease in selectivity is less when gold is present in the membrane.

Table 7. Ratio of H₂ permeance under H₂S exposure and without H₂S (initial value) at different H₂S contents in H₂ feed and at 550 °C, and final H₂/N₂ ideal perm-selectivity after H₂S tests [31].

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>Ratio of H₂ permeance under H₂S compared to initial value</th>
<th>Final H₂/N₂ ideal perm-selectivity after H₂S tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>E505 PdAg</td>
<td>38.1% 39.0% - -</td>
<td>18</td>
</tr>
<tr>
<td>E505 PdAgAu (5% Au)</td>
<td>51.2% 55.6% 54.0% -</td>
<td>793</td>
</tr>
<tr>
<td>E506 PdAgAu (7% Au)</td>
<td>74.4% - 64.8% 60.1%</td>
<td>121</td>
</tr>
</tbody>
</table>

3.2. Membrane reactor test results

3.2.1 WGS membrane reactor

The performance of a fluidized bed WGS membrane reactor (FBMR) using five ceramic supported Pd-Ag membrane (4-5 µm) has been investigated at different pressures from 1–2.5 bar and compared with the performance of a conventional fluidized bed reactor (FBR) [30]. The CO conversion of the FBR is considered as the reference case, which is compared to the case of a fluidized bed with internals (FBR, w) where the membrane module is just immersed but no gas is extracted via the membranes, and the case of a fluidized bed membrane reactor (FBMR) with extraction via the membranes. In one of the tests the inlet flow rate was kept constant. Figure 10 clearly shows higher CO conversions at higher membrane reactor pressures when keeping the inlet flow rate constant. In this case at higher pressures the hydrogen recovery will be higher as well (average CO impurity: 7 ppm, min: 3 ppm, max: 9 ppm). Although increasing the pressure above 2 bar inside the reactor did not affect the performance of the membrane reactor much. This is due to the fact that at higher pressures (with constant inlet flow rate) the U/Uₘᵣ ratio will be lower. Therefore, at higher pressures the mixing will be worse and this will induce the mass transfer limitation inside the catalytic bed. Although CO conversions above the equilibrium can be achieved for higher inlet flow rates, due to limitations in the CO mass flow controller, experiments for higher inlet flow rates were not feasible with the specified inlet gas composition. Therefore, experiments were continued with a semi-industrial WGS inlet gas composition.
Figure 10. Membrane reactor performance at different pressures up to 2.5 bar and at 400 °C, CO (5%), H₂O (15%), CH₄ (0%), H₂ (18%), N₂ balance, U/Umf: 1.71–6, Ppermeate: 30 mbar [30].

Figure 11 shows the reactor performance results by feeding a semi-industrial WGS feed composition (WGS gas as outlet of a steam methane reformer) at different pressures. The inlet flow rate was kept the same for all the cases to keep the ratio of the inlet flow rate to the membrane area constant, as in the previous study. The obtained results confirmed the better performance of the membrane reactor at higher pressures, although the maximum total pressure was 2 bar due to limitations with the current setup. The CO content in the permeate is below 10 ppm (average CO impurity: 5.6 ppm, min: 4.5 max: 7 ppm), which guarantees the H₂ quality for fuel cell applications. The H₂ production obtained with 5 sealed membranes was up to 0.1 Nm³/h.

Figure 11. Membrane reactor performance for a semi-industrial inlet composition at 400 °C, CO (9.2%), H₂O (19%), CH₄ (4%), H₂ (30%), N₂ balance, U/Umf: 1.67-5, Ppermeate: 30 mbar [30].
3.2.2 Steam methane reforming membrane reactor

In this section the performance of module containing five tubular membranes prepared by TECNALIA (4 μm Pd-Ag layer deposited onto ZrO₂) has been evaluated under steam methane reforming conditions (SMR) and compared to the case when using commercially available thicker Pd membranes from REB [23]. Figure 12 shows the flue gas composition and the methane conversion at 550 and 600 °C at a steam to carbon ratio of 3. It can be seen that methane conversion increases with increasing temperatures, where the extracted hydrogen stream includes a noticeable amount of CO, although hydrogen purity remains above 99.98% for all cases. A summary of the different operating conditions and results over the days is also reported in Figure 12. During the experiments it was measured an increase in the fuel conversion as compared to the thermodynamic equilibrium. Analyzing the surface of the membranes and the sealing after these tests, it was observed that the sealing was damaged, which explains the CO increase in the permeate gas stream. On the other hand, the membrane surface was free of defects, which assures that the membranes can survive under reforming conditions for this test duration.

Autothermal reforming of methane is another process tested with the ceramic supported thin-film Pd based membranes presented above and the results were compared to commercially available membranes. Comparing the results obtained with the membrane reactor to the conventional fluidized bed, an increase in conversion (from 89.5% to 96.7%) was observed. Furthermore, the hydrogen recovery obtained with the thin membranes was much higher (35%) as compare to the recovery that can be achieved with commercial membranes (20%). This is associated to the large increase in hydrogen permeations related to the thickness of the Pd layer [44]. On the other hand, it is more probable that these thin membranes, under fluidization conditions are more prone to become damaged, showing a decrease in the purity of the permeated hydrogen and hindering its use in ultra-pure hydrogen applications like in fuel cells. Actually, it has been verified experimentally that the impurities (mostly CO) measured during reaction were >500 ppm, whereas in the case of thick commercial membranes the impurities were hardly detected (<1.5 ppm). In these membranes it was confirmed that leakages were coming from the sealing of the membrane with a metallic tube using the graphite ferrules. Some conclusions regarding the use of ceramic supported membranes can be obtained after all these tests. For instance, it is observed that still more research is needed regarding sealing methods for these membranes, especially if they will be integrated in membrane reactors and the main purpose of the system is the production of ultra-pure hydrogen. For this, more robust ceramic supports (for example, thicker wall tubes) are needed to improve the mechanical stability and to withstand possible vibrations during fluidization. In addition, a higher torque can be applied onto the
Pd membranes supported on thicker ceramic tubes when using the sealing method thereby reducing the leak rate through the sealing; also, changing the geometry of the graphite seals could improve the performance. On the other hand, other type of sealing methods could be investigated (e.g. brazing) that can improve the leak tightness and reduce the sealing cost. Moreover, longer membranes (e.g. up to 100 cm) should be produced as this would decrease the number of sealings and thus also decrease possible leakages and simplify the assembly of the membrane reactors without compromising the mechanical stability of the membrane. However, if these membranes will be placed downstream in the process as separation units, moderated temperatures are required to ensure stability over time to be able to substitute conventional and fully developed technologies like PSA.

On the other hand, the performance of a metallic supported thin Pd-Ag membrane (4-5 µm thick Pd-Ag membrane deposited onto ceramic coated Hastelloy X porous support) for reaction tests in a fluidized bed membrane reactor is presented [25]. Steam methane reforming and autothermal reforming of methane processes have been investigated first in a conventional fluidized bed and subsequently in the membrane reactor. The two systems were studied at different operating conditions (viz. temperature, pressure, steam to carbon ratio, etc) and for all cases it was demonstrated that the membrane reactor clearly outperforms the behaviour in the fluidized bed. The results of these studies are presented in Figure 13. It is worth noting that in all the cases it is observed an increase in fuel conversion when hydrogen is selectively removed from the bed. Furthermore, to allow a better interpretation of the data, calculated thermodynamic equilibrium lines have been included in the figures to visualize that the membrane reactor configuration clearly goes beyond this thermodynamic restriction. For almost all cases it is observed that thermodynamic equilibrium is achieved in the fluidized bed reactor configuration (without membrane) and that, after changing the configuration to a fluidized bed membrane reactor, the conventional equilibrium restriction is circumvented.

![Figure 13](image-url)

**Figure 13.** Methane conversion as a function of temperature and pressure for the two reactor configurations studied fluidized bed reactor (FBR) and fluidized bed membrane reactor (FBMR) using metallic supported Pd-Ag membrane, for steam methane reforming and autothermal reforming [25].

Although better performances were obtained in the membrane reactor configuration, still the desired hydrogen purity was not achieved (impurities > 800 ppm). However these impurities allowed the discovery of a beneficial fact of metallic supports. Surprisingly, in presence of CO, they show catalytic activity [25], mainly methanation reaction, thus leading to a decrease in the concentration of CO and CO$_2$ in the permeate side with the corresponding increase in CH$_4$ concentration. If this permeate stream is sent to a fuel cell for energy generation, CO would poison the system leading to very low efficiencies [45]. However, CH$_4$ hardly shows an influence on the fuel cell efficiency and thus the catalytic activity of the support could be considered as an additional advantage of membrane reactors.
4. Conclusions

The present work shows a summary of the performance of different Pd-based supported membranes (on various supports and with different thicknesses) for their use in membrane reactors for hydrogen production. 4 microns thick Pd-Ag membranes supported on ceramic tubes presented a high H₂ permeance (≈4 x 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹) and a high H₂/N₂ ideal selectivity (10000-20000) at 400 °C and 100 kPa for 900 h. 4-5 µm thick Pd-Ag membranes supported on ceramic coated metallic supports were also prepared: one membrane was tested at 400 °C and 3 bar of pressure difference for 1,200 h showing extremely high ideal H₂/N₂ selectivity (>150,000) and moderate H₂ permeance (9.0 x 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹). Another similar membrane has been tested above 550 °C presenting stable H₂ permeance but after some hours a decrease in the H₂/N₂ selectivity was observed due to the increase in N₂ permeance. The N₂ permeance increase was associated to small defects formed on the surface. Thus, long-term stability at high temperatures (>500 °C) needs to be improved. A 1.3 µm thick Pd-Ag deposited by simultaneous electroless plating and supported onto a ceramic porous tube showed a H₂ permeance of 9.0-9.4 x 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ with a H₂/N₂ ideal perm-selectivity of 1900 after 1000 hours of operation at 400 °C and 1 bar. Pd-Ag membranes prepared by direct PVD-MS technique onto ceramic porous supports showed low H₂/N₂ selectivity (due to the very high N₂ permeance) but when depositing a thin Pd layer by ELP onto the PVD-MS layer the H₂/N₂ ideal perm-selectivity was 500 with a very high H₂ permeance of 8 x 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ at 400 °C and 100 kPa. The different performance of the membranes (in terms of H₂ permeance and H₂/N₂ ideal perm-selectivity) gives the possibility to choose the suitable membrane depending on the required H₂ purity for a certain application. Pd-Ag-Au membranes showed an enhanced resistance to H₂S content (in ppm) compared to Pd-Ag membranes, and they could be used for H₂ production by reforming a natural gas or biogas containing H₂S.

On the other hand, ceramic supported Pd-Ag membranes (4 µm) have been tested in a fluidized bed WGS membrane reactor showing an improvement on CO conversion compared to the conventional fluidized bed reactor (without membranes). The CO content in the permeate is below 10 ppm, which guarantees the H₂ quality for PEM fuel cells. SMR and ATR reactions carried out with ceramic and metallic supported Pd-Ag membranes showed significant improvement in the performance compared to conventional reactors (without membranes) and to membrane reactors using commercial thicker membranes (e.g. Pd membranes from REB). The long-term stability at high temperatures of the Pd-based supported membranes is still an issue and it should be improved for bringing this type of membranes and membranes reactors to the market.

Acknowledgments

The presented work is funded within DEMCAMER (nº NMP3-LA-2011-262840), ReforCELL (nº 278997), FERRET (nº 621181) and FluidCELL (nº 621196) projects as part of the European Union’s Seventh Framework Programme (FP7/2007-2013) and for the Fuel Cells and Hydrogen Joint Technology Initiative. This project has also received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No 671459 (BIONICO). This Joint Undertaking receives support from the European Union’s Horizon 2020 research and innovation programme and Italy, Spain, Netherlands, United Kingdom, Germany, Portugal, Switzerland. This work is also funded within MEMPORE project (PI_2014_1_25) given by the Basque Department of Education, Language policy and Culture. The authors would like to thank University of Basque Country (UPV-EHU) for Zabalduz scholarship program. The authors would also like to thank Rauschert Kloster Veilsdorf for providing the ceramic tubular supports and Johnson Matthey for providing the catalysts.
Disclosure: The present publication reflects only the author’s views and the FCH JU and the Union are not liable for any use that may be made of the information contained therein.

References


