October 2004 ECN-RX--04-093

MEMBRANES FOR HYDROGEN PRODUCTION WITH CO_2 CAPTURE

Paper and poster presented at the Seventh International Conference on Greenhouse Gas Control Technologies (GHGT-7) in Vancouver, Canada 5th -9th September, 2004

P.P.A.C. Pex
Y.C. van Delft
L.A. Correia
H.M. van Veen
D. Jansen
J.W. Dijkstra

Acknowledgement

The authors gratefully acknowledge the financial support of the Dutch Ministry of Economic Affairs (EZ), EDI programme (EDI03202, Senter) and the European Commission of the work presented.

Abstract

Hydrogen membrane reactors have been identified as a promising option for power production with CO_2 capture. Hydrogen selective Pd/Ag membranes are expected to play a key role in the development of more advanced process schemes for Pre-Combustion De-Carbonisation. This poster gives an overview of the results and current status of the membrane development as part of the R&D trajectory of hydrogen membrane reactors at ECN.

Dense tubular membranes with very thin Pd/Ag layers have been made on ceramic supports with electroless plating on a 1 m^2 scale. Measurements have shown that after initial activation very high hyrogen permeances can be obtained with high selectivities. The membrane has been on stream for 70 days using simulated reformate gas and showing an acceptable performance. The roadmap for further development has been determined and results up to now are very encouraging.

CONTENTS

1. INTRODUCTION

A sustainable use of fossil fuels in the future will undoubtedly make use of concepts where the energy content of the fossil fuel is transferred to hydrogen. The driving force for these concepts is the possibility of capturing CO_2 elegantly while using the favourable thermodynamics to increase the efficiency of hydrogen production significantly. At the Energy research Centre of the Netherlands ECN an R&D programme DECAFF (De-CArbonisation of Fossil Fuels) is being carried out which has a focus on the development of advanced technologies for power generation with CO_2 capture. The aim is to reduce the CO_2 capture efficiency penalty with 50% and the financial penalty with 40%. In ECN's vision membranes will play a key role in future decarbonisation of fossil fuels. An overview of the current status of the membrane development as part of the R&D trajectory of hydrogen membrane reactors at ECN is presented.

2. SYSTEMS FOR PRE-COMBUSTION DECARBONISATION WITH MEMBRANE REACTORS

Combining reaction and separation using membrane reactors has been shown to offer numerous advantages for hydrogen production with CO_2 capture, also referred to as Pre-Combustion De-Carbonisation (PCDC). The application of hydrogen selective membranes for the removal of hydrogen from reforming and shift reactions gives higher conversion of these equilibrium reactions at lower temperatures. The remaining gas consists predominantly of CO_2 and excess steam at a relatively high pressure, which can be stored in geologic formations after condensation of the steam. With this technology the CO_2 emissions of conventional power plants can be reduced with up to 75%. Moreover membrane technology is key to more advanced process schemes. Several process schemes have been proposed in literature for climate neutral electricity production using hydrogen membrane reactors. They all exhibited certain key elements like fuel treatment, a water gas shift reaction, hydrogen separation with membrane reactors, water removal and CO_2 sequestration. The electricity production step can be done with a variety of conventional and advanced technologies like gas turbines (GTs) and fuel cells (SOFC). The shift membrane burner (SMB)/SOFC combination and the membrane reformer placed in a GT cycle have been proposed and discussed in [1], [2], [3]. ECN develops thin layer palladium alloy membrane technology for PCDC concepts because this technology is expected to reduce the cost of CO_2 avoided to a level < 25 €/ton.

3. MEMBRANE DEVELOPMENT

In steam reforming and water gas shift processes membrane separation can be economical viable using current thin layer palladium alloy membrane technology, however a further increase in flux and/or decrease in membrane price is absolutely needed to convince the process owners of the suitability of this promising technology. Membrane development at ECN focuses on the development of thinner and cheaper metallic membranes with higher permeation rates. Dense Pd/Ag membranes consist of a very thin layer of alloy supported by a porous inorganic substrate. The Pd/Ag membranes are made by electroless plating. Pure (gas-tight) palladium layers can be prepared varying in thickness between 0.5 and 4 micron. Silver is deposited on top of the thin pure Pd-membrane and sintered to obtain the required alloy composition. By optimising the electroless plating technique it is possible to manufacture membrane layers (Pd/23%Ag) with a thickness of 3 to 5 micron on ceramic supports (see Figure 3.1).

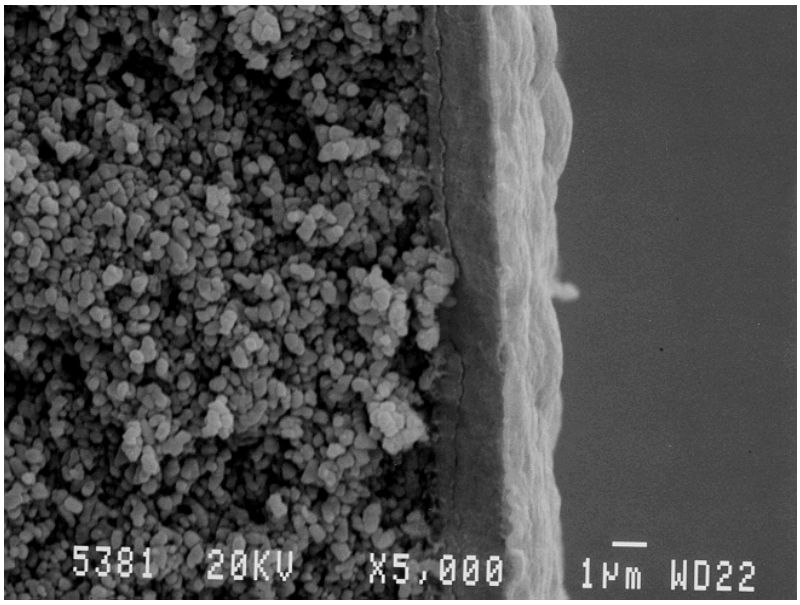

Figure 3.1 *SEM cross section of fractured sample of Pd/23%Ag membrane layer on ceramic support*

Using the above described procedure membrane tubes with a length of 0.8 meter and an outer diameter of 14 mm can be prepared reproducibly on a regular basis [4]. 24 of these comprise about 1 m^2 of membrane area. He leak tests show that the prepared and sintered membranes are gas-tight. In Figure 2 a photograph is given of these membranes. After activation the majority of the membrane samples have been used for single gas permeance tests at different temperatures and for the separation of hydrogen from reformate gas, using a bench scale test system that can operate up to 500ºC and 65 bar feed pressure with a membrane area of about 50cm^2. Before and after each test with reformate gas single gas permeance tests at 350ºC using hydrogen and nitrogen have been done in order to monitor changes in the membranes performance and to determine the issues for further improvement.

Figure 3.2 *Set of membrane tubes with a length of 0.8 meter for the separator unit*

4. MEMBRANE TEST RESULTS AND DISCUSSION

Results of bench scale hydrogen permeance tests at different temperatures are presented in Figure 3.3. [5] The dense membranes show high hydrogen fluxes of up to 105 $m^3/m^2hbar^{0.5}$ at 400ºC. At low feed pressures no nitrogen flux was detected and if the detection limit of the equipment is taken as the measured nitrogen flux, then the permselectivity is > 1000. At high feed pressures the permselectivity was around 300 indicating a leak flow through the sealing. Tests with simulated reformate gas at 350ºC gave lower selectivities due to lower hydrogen permeances caused by the poisonous CO in the reformate gas.

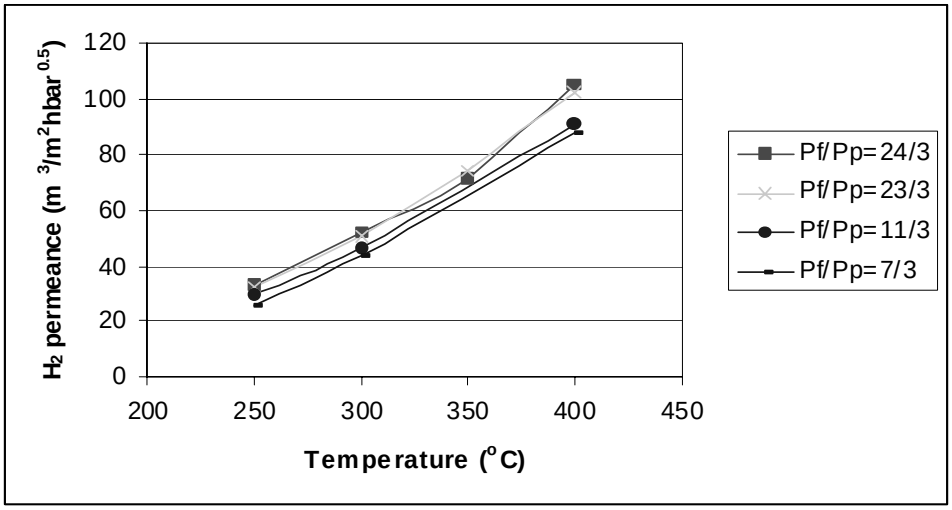

Figure 4.1 *Hydrogen permeance at different temperatures (Pf= feed pressure, Pp=permeate pressure, pressures in barg)*

The membrane has been on stream for about 70 days using simulated reformate gas under different process conditions and its performance is shown in Figure 3.4.

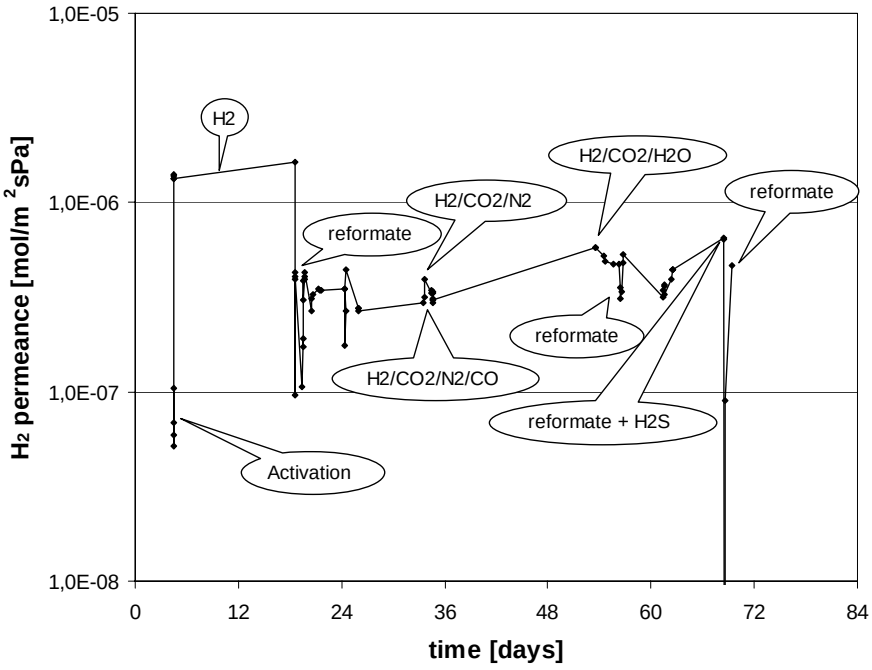

Figure 4.2 *H_2 permeance vs. time on stream (T=350ºC, Pfeed= 23 - 45 bara)*

After a rapid decrease during the first separation tests, the hydrogen permeance decreases slowly reaching a stable performance. The permselectivity dropped after the first separation tests, but directly after measurements with sweep flow the permselectivity increased.

Further development is focussed on the large scale manufacturing of palladium alloy membrane layers applied onto stainless steel supports having inorganic intermediate layers. Cost-effectiveness in the envisaged applications is the main driver for this development and gives direction to all relevant technical aspects in this development such as reproducible manufacturing techniques, improvement of long-term stability and prevention of performance decrease due to poisonous adsorbing gas components such as CO or sulphur. Results thus far in membrane reactor tests encourage us to proceed in the route that has been taken. This membrane development is part of a programme in which system development (membrane reactor design, hydrodynamics, dynamic reaction engineering) and process development (process schemes, process performance targets) are leading us towards the availability of energy-efficient hydrogen membrane reactors for effective CO_2 capture.

5. CONCLUSIONS

Membrane reactors with hydrogen selective Pd/Ag membranes have been identified as a promising option for power production with CO_2 capture. Dense tubular membranes with very thin Pd/Ag layers have been made on ceramic supports with electroless plating on a $1m^2$ scale. Measurements have shown that after initial activation very high hydrogen permeances can be obtained with high selectivities. The membrane has been on stream for 70 days using simulated reformate gas and showing an acceptable performance.

The roadmap for further development has been determined and results up to now are very encouraging. We are interested to team up with groups or organisations that are positioned to contribute effectively to our programme.

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