October 2004 ECN-RX--04-096

PALLADIUM ALLOY MEMBRANES FOR ENERGY EFFICIENT MEMBRANE REACTORS

Proc. of the 8th International Conference on Inorganic Membranes Cincinnati, July 18-22, 2004. p. 524-527

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 contributions of our partners in the EU Joule project JOE3-CT97-0075 and partly financial support of the Dutch Ministry of Economic Affairs (EZ), EDI programme (EDI03202, Senter) and the European Commission of the work presented.

Abstract
In ECN's vision hydrogen separation membranes will play a key role in future power production systems and industrial chemical production processes. The driving force for the application of these membranes is that during reaction favourable thermodynamics can be utilised to increase efficiency while elegantly CO_2 can be captured under high pressure or chemical products can be obtained cost-effectively.
Applications envisaged and currently investigated are:

- process integrated hydrogen membrane reactors for reforming, water gas shift and production of paraffins with parallel removal of hydrogen,
- small-scale efficient hydrogen production with membrane reactors,
- hydrogen recovery from industrial (waste) streams.

In the above processes membrane separation can only be economically 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 hydrogen permeation rates. Important activities concern the development of reproducible manufacturing techniques for porous stainless steel supported thin layer palladium alloy membranes, improvement of long-term stability and prevention of performance decrease due to poisonous adsorbing gas components such as CO or sulphur. The research is guided and supported by advanced process studies and flowsheet calculations using membrane reactor simulators and membrane reactor testing under simulated realistic conditions. This poster gives an overview of the results and current status of the membrane materials development as part of the R&D trajectory of hydrogen membrane reactors at ECN.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

In ECN's vision hydrogen separation membranes will play a key role in future power production systems and industrial chemical production processes. The driving force for the application of these membranes is that during reaction favourable thermodynamics can be utilised to increase efficiency while elegantly CO_2 can be captured under high pressure or chemical products can be obtained cost-effectively.

Applications envisaged and currently investigated are:

- process integrated hydrogen membrane reactors for reforming, water gas shift and production of paraffins with parallel removal of hydrogen,
- small-scale efficient hydrogen production with membrane reactors,
- hydrogen recovery from industrial (waste) streams.

In the above processes membrane separation can only be economically 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 hydrogen permeation rates. Important activities concern the development of reproducible manufacturing techniques for porous stainless steel supported thin layer palladium alloy membranes, improvement of long-term stability and prevention of performance decrease due to poisonous adsorbing gas components such as CO or sulphur. The research is guided and supported by advanced process studies and flowsheet calculations using membrane reactor simulators and membrane reactor testing under simulated realistic conditions. This poster gives an overview of the results and current status of the membrane materials development as part of the R&D trajectory of hydrogen membrane reactors at ECN.

1. EXPERIMENTAL

The membrane development was started by evaluating six different manufacturing techniques: Magnetron sputtering, metal organic chemical vapour deposition, electroless plating, laser deposition, pore plugging by in-situ reduction and pore plugging with micro-emulsions. An evaluation of the progress in all six membrane-manufacturing routes was made in the framework of a project funded by the European Commission. The criteria against which the evaluation was done were performance, stability, production cost, ease of production, raw materials cost, impact on environment, possible improvements on short term. The relative overall ranking of the evaluation is given in the next table.

Table 1.1 *Relative overall ranking of the evaluation*

Membrane manufacturing technique	Ranking
Electroless plating	1
Pore plugging – interfacial reaction	0.77
Pore plugging – micro emulsion technique	0.72
Magnetron sputtering	0.63
Laser deposition	0.52
Chemical vapour deposition	0.46

It was decided to continue only with the electroless plating technique. A dedicated optimisation programme was elaborated and the research aspects concerned performance improvement, manufacturing cost reduction and further durability and lifetime improvement.

By optimising the electroless plating technique it was possible to manufacture membrane layers (Pd/23%Ag) with a total thickness of 3 to 5 µm on ceramic supports (see Figure 1.1).

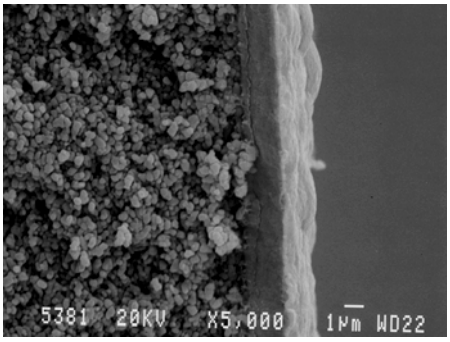

Figure 1.1 *SEM cross section of fractured sample of Pd/23%Ag membrane layer on ceramic support*

The alloying of the membrane layers was done by sequential plating of palladium followed by silver. The necessary amount of silver to obtain a Pd/23%Ag layer was calculated from the amount of palladium, which was deposited in the first step. The operating window for depositing the right amount of silver was determined experimentally. After deposition it was necessary to make the alloy by heat treatment. Using the above described procedure 24 membrane tubes with a length of 0.8 meter and an outer diameter of 14 mm have been prepared. This comprises about 1 m^2 of membrane area. He leak tests show that the prepared and sintered membranes are gas-tight. In Figure 1.2 a photograph is given of this set of 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.

Figure 1.2 *Set of 24 membrane tubes with a length of 0.8 meter for the separator unit*

2. RESULTS AND DISCUSSION

Results of bench scale hydrogen permeance tests at different temperatures are presented in Figure 2.1. 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.

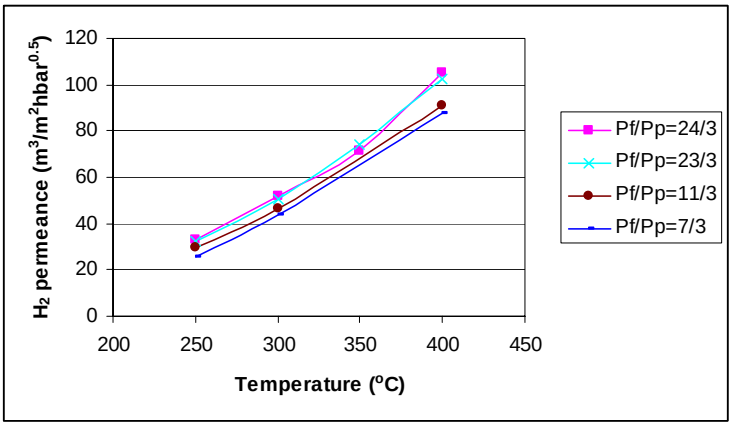

Figure 2.1 *Hydrogen permeance at different temperatures (Pf= feed pressure, Pp=permeate pressure, pressures in barg)*

The membrane has been on stream for about 55 days using simulated reformate gas under different process conditions and its performance is shown in Figure 2.2.

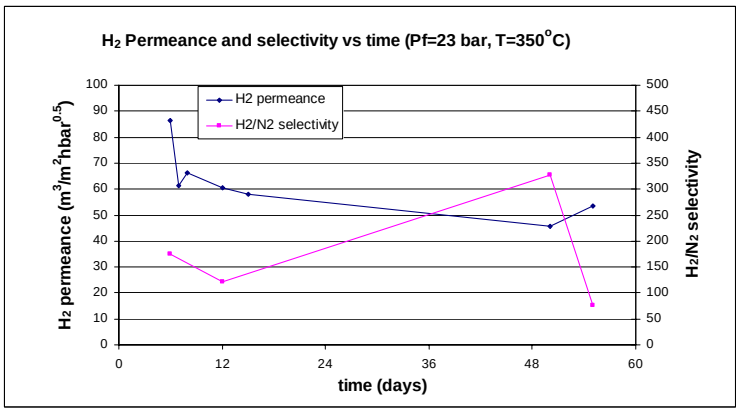

Figure 2.2 *Hydrogen permeance and H_2/N_2 permselectivity vs. time on stream*

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 manufacturing procedures,

permeance (a.o. membrane thickness, poisoning), selectivity (a.o. zero defect manufacturing of extremely thin layers), longevity (a.o. alloy composition and homogeneity of it). 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.

3. CONCLUSION

Dense tubular membranes with very thin palladium silver 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 55 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.