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MEMBRANES FOR HYDROGEN PRODUCTION

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Acknowledgement/Preface

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Abstract

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. Separation of hydrogen using membranes can play an important role in purification and process intensification of hydrogen production technologies.

In ECN's vision membranes can play a key role in future hydrogen production systems. 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.

Applications envisaged that are currently investigated are:
- hydrogen recovery from industrial (waste) streams,
- hydrogen membrane reactors for water gas shift with parallel removal of hydrogen,
- small-scale efficient hydrogen production with membrane reactors.

An overview of results of membrane and system development on above applications is presented.

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1. MEMBRANE DEVELOPMENT

Membrane development at ECN focuses predominantly on the development of tubular asymmetric (layered) systems where the membrane layers are (micro) porous as well as dense (metallic and ceramic).

Microporous silica membranes are made in a batch process, with a maximum of 10 tubes each time. The membrane tubes are made at a length of 1 meter and an ID/OD of 8/14 mm. The pore size of the membranes is about 5Å and can be optimised for certain applications by e.g. modifying the silica sol or the calcining procedure. The separation layer of these membranes consists of a very thin (<200 nm) hydrophilic amorphous silica film on the outside of a multi-layer alumina support tube (see Figure 1). At 350ºC H_2 permeances range from 1 to 3 10^{-6} mol/m^2sPa and H_2/CO_2 permselectivities up to 39.

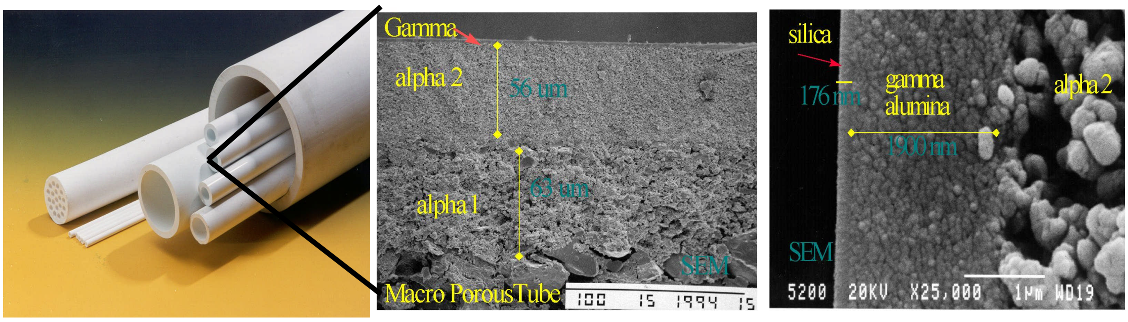

Figure 1.1 *SEM micrographs of silica membranes and membrane layers*

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 a thin pure Pd-membrane and sintered to obtain the required alloy composition. Prototype membranes are available with lengths up to 1 meter (see Figure 2). Permeation measurements at 350ºC with Pd/23%Ag membranes show a very high hydrogen flux (1-3 10^{-6} mol/m^2sPa) increasing in time (as a result of increasing alloying) whereas no nitrogen or other components flux can be detected.

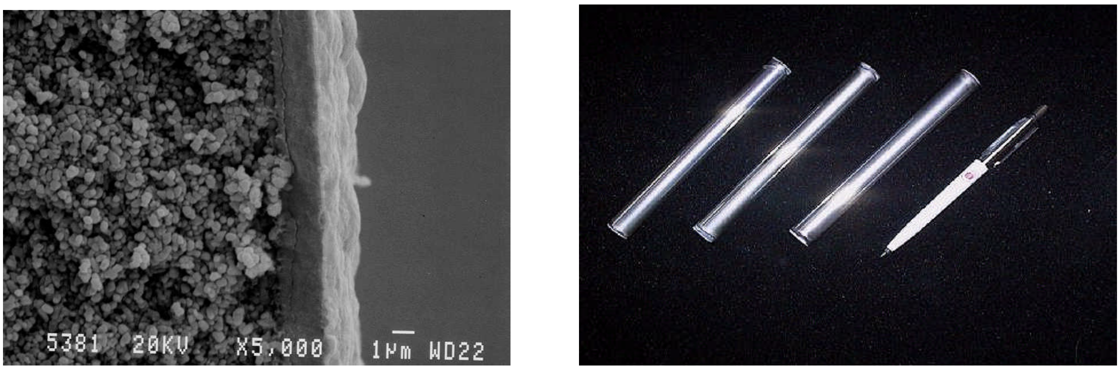

Figure 1.2 *Membranes made with electroless plating: SEM cross-section and overview of tubes*

2. FEASIBILITY STUDY HYDROGEN SEPARATION WITH MEMBRANES

As an important component in the chemical industry, hydrogen takes part in many processes. The feasibility of inorganic membranes for hydrogen separation in chemical processes was studied. In several of the processes studied the application of inorganic hydrogen selective membranes will lead to benefits in the process and thereby increase the energy efficiency of the overall process. In steam reforming and water gas shift processes membrane separation can be economic feasible. There is a large potential for using the membranes as CO_2 abatement technology. For a rather small size (400 MW) coal fired power plant the CO_2 emissions can be reduced with 1640 kton/year, being 75% lower than in conventional plants.

For the application of hydrogen selective membranes for shifting the equilibrium of the steam reformer reaction in ammonia and methanol production processes the economics are not yet viable. The selectivity demands for the membranes in the processes can be reached with nowadays available membranes, however, an increase in flux and/or a decrease in membrane price would be more convincing to the process owners. The water and high temperature stability of the membranes still needs to be improved. The availability of these membranes could lead to an energy reduction of about 15 PJ/year in the Netherlands or 840 kton/year less CO_2 emissions.

3. WATER GAS SHIFT MEMB RANE REACTOR MODELLING

A software model of the water gas shift membrane reactor has been developed. The model simulates a counter current water gas shift membrane reactor with microporous membranes (silica and zeolite) and dense (palladium and proton conducting) membranes and copes with the isothermal and non-isothermal operation of the membrane reactor (Figure 3). The membrane reactor model is implemented as an Aspen Plus User Model (Aspen Plus, version 11.1) and is written in FORTRAN. A temperature dependent hydrogen permeance has been incorporated. The model is used for detailed evaluation of the performance of different inorganic membranes in the water gas shift reaction in combination with e.g. coal gasification or steam reforming.

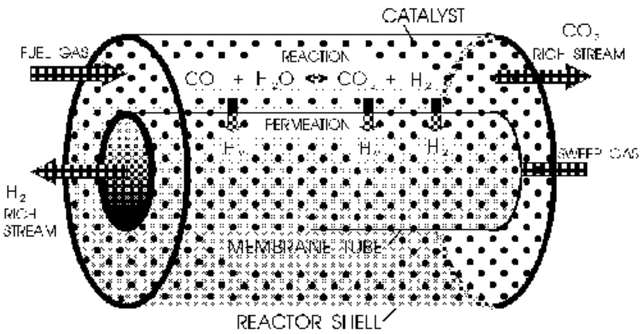

Figure 3.1 *Schematic representation of a WGSMR*