

Catalytic Membrane Reactor for Dehydrogenation of Water Via Gas-Shift: A Review of the Activities for the Fusion Reactor Fuel Cycle

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Abstract : Pd-ceramic composite membranes and catalytic membrane reactors (CMR) have been studied for hydrogen and its isotopes (deuterium and tritium) purification and recovery in the fusion reactor fuel cycle. Particularly, a closed-loop process has been studied for recovering tritium from tritiated water by means of a CMR in which the water gas shift reaction takes place. The development of the techniques for coating micro-porous ceramic tubes with Pd and Pd/Ag thin layers is described: composite membranes have been produced by electroless deposition (Pd/Ag film of 10-20 μm) and rolling of thin metal sheets (Pd and Pd/Ag membranes of 50-70 μm). Experimental results of the electroless membranes have shown a not complete hydrogen selectivity because of the presence of some defects (micro-holes) in the metallic thin layer. Conversely, the rolled thin Pd and Pd/Ag membranes have separated hydrogen from the other gases with a complete selectivity giving rise to a slightly larger (about a factor 1.7) mass transfer resistance with respect to the electroless membranes. Experimental tests have confirmed the good performances of the rolled membranes in terms of chemical stability over several weeks of operation. Therefore, these rolled membranes and CMR are adequate for applications in the fusion reactor fuel cycle as well as in the industrial processes where high pure hydrogen is required (i.e. hydrocarbon reforming for fuel cell).

1. Introduction

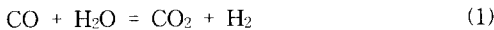
The membrane technologies have been proposed for applications in the fusion reactor fuel cycle, i.e. fuel purification and waste processing, in alternative to the traditional processes based on molecular sieves or cryogenic traps [1-5].

The CMR with Pd-ceramic composite membranes has been studied to separate and recover hydrogen and its isotopes from tritiated water. For the applications in the fusion reactor fuel cycle, a mandatory requirement is the complete hydrogen selectivity (permselectivity) of the membranes, in order to avoid tritium losses. Since

the beginning of the '90s, ceramic porous tubes have been coated with thin layers (10 μm) of Pd-Ag by a modified electroless technique [6,7]. These membranes have shown high separation factors (10-100) but not a complete hydrogen selectivity. Thus, these membranes are suitable for industrial applications such as hydrogenation/dehydrogenation of hydrocarbons but do not fit well the nuclear applications: studies for improving the quality of the metallic layer are in progress. In the last years, in order to obtain permselective Pd based membranes thinner than the commercial ones (100-150 μm) a procedure of cold-rolling and annealing of metal sheets

has been developed [8-10]. Rolled Pd and Pd-Ag membranes have been produced with thickness in the range 50-70 μm : these membranes have exhibited a slightly lower permeance than the electroless membranes but, conversely, are characterized by a complete hydrogen selectivity. Consequently, these membranes are suitable for applications in the fusion reactor fuel cycle as well as in industrial processes, where high pure hydrogen production is required, i.e. hydrocarbon reforming for fuel cells.

These membranes have been studied for a closed-loop process with reference to the ITER (International Thermonuclear Experimental Reactor) design [9]. In this process a CMR is proposed to recover hydrogen isotopes in elemental form from tritiated water by using a catalyst selective for the water-gas shift reaction:



In this process the consumption of CO and the large production of CO_2 contaminated wastes are avoided. The main advantages of the process consist in the possibility of reducing the number of process items and controls and the tritium inventory, and then increasing both the reliability and safety of the fuel cycle plant.

2. Electroless Membranes

Composite membranes, composed of a thin film of Pd/Ag alloy (10 μm thick) supported by a porous ceramic tube, see scheme in Fig. 1, have been produced with a modified electroless technique [6,7]. The selected support is a commercial macro-porous tube of Al_2O_3 (average size about 12 μm) with the following dimensions: length 250 mm, outside diameter 10 mm, inside diameter 7 mm. In order to guarantee the deposition of the PdAg film, the dimension of the external pores is reduced by vacuum aspiration of an alumina powder (size 0.1-1 μm) suspension with polyethylenglykol in water. When a permeance value $\text{Pe}=0.5 \times 10^{-6} \text{ m}^3/\text{m}^2 \text{ s}$

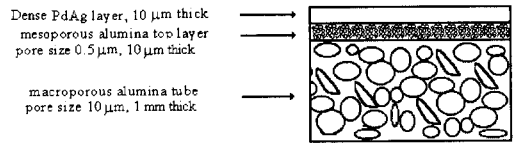


Fig. 1. Scheme of an electroless membrane.

Pa is reached, a thermal treatment is carried out. After two more cycles of aspirations, drying at 120°C and thermal treatments at 1200°C, a stable permeance value $\text{Pe}=0.5 \times 10^{-6} \text{ m}^3/\text{m}^2 \text{ s Pa}$ is obtained.

Ceramic membranes produced in this way have shown, at SEM analysis, external pore size of 0.5 μm . In order to activate the ceramic surface for the electroless plating deposition an activation bath having the following composition has been used: PdCl_2 : 0.68 g/l, SnCl_2 : 4.75 g/l, HCl conc.: 100 ml/l.

After this critical step, a classical palladium and silver electroless depositions are carried out. Once palladium and silver have been deposited in proper ratios (Pd 77%, Ag 23%) a heat treatment performed at 650°C for 5 days ensures the achievement of the palladium-silver alloy. Then the composite membrane has been water-proofed at the edges by an end-sealing treatment based on a glassy coating.

An improvement in the deposition technique is presently required as some microscopic defects (micro-holes) have been found on metallic surfaces, although the deposited film is always well sticking to the support.

3. Rolled Membranes

Thin Pd-based rolled membranes (50-70 μm), see scheme in Fig. 2, have been developed in order to obtain a metallic layer thick enough to avoid defects of the metallic layer, and ensure a complete selectivity without giving large mass transfer resistance with respect to the electroless membranes.

Thin Pd and Pd/Ag sheets have been cold-rolled by a two-high laboratory mill [9,10].

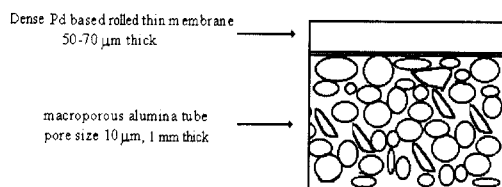


Fig. 2. Scheme of a rolled membrane.

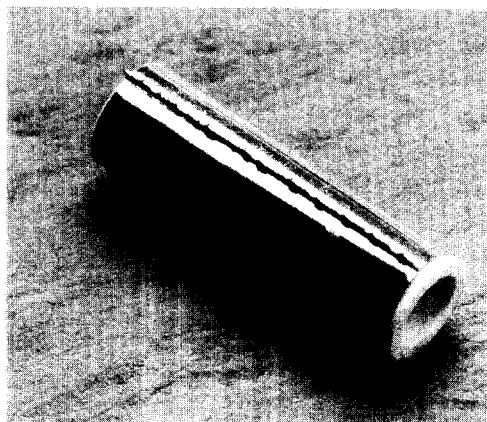


Fig. 3. A specimen of a rolled membrane.

Several steps of cold rolling and annealing of the palladium and palladium silver foils have been necessary in order to relieve the mechanical stresses due to the work hardening upon rolling, particularly for the alloyed palladium. Measurements of Vicker hardness have been carried out during the rolling process in order to characterize the hardening status and to evaluate the workability of the specimens before going on to the annealing step. Annealing of the metal palladium and alloy foils has been carried out by heat treatment in a furnace at 1200°C and atmospheric pressure for 2-3 hours under Ar atmosphere to avoid oxidation and tarnishing of the palladium surfaces.

After rolling the metallic foils have been closed by TIG arc welding in order to obtain two permeating tubes of 150 mm length, 10 mm internal diameter and 70 (for Pd) and 50 μm (for PdAg) thickness. A sample of a rolled membrane is shown in Fig. 3. At the ends of the metallic membranes two stainless steel tubes,

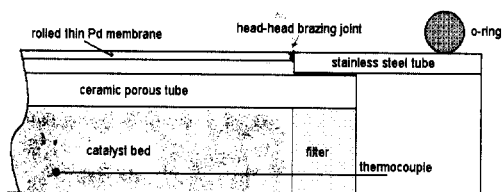


Fig. 4. Scheme of a CMR with a rolled membrane.

100 μm thick, have been jointed by brazing in order to reach, under operating conditions, a thermal gradient able to reduce the temperature in the o-ring zone of the reactor. Finally a porous ceramic tube, containing the catalyst bed in the CMR version, has been put inside the metallic membrane to avoid any contact between the palladium and the catalyst, as shown in scheme of Fig. 4.

4. Pd-Ceramic Membrane: Modeling and Process Applications

A mathematical model of a CMR for the water gas shift reaction and a computer code, WGSR, have been developed [8]. The code WGRS has proved to be a useful tool to understand the processes occurring in the CMR, to find the optimum operating conditions in the processes studied for the fusion fuel cycle, and to foresee the results of the experimental tests.

4.1. Computer Code

The model is based on the following main assumptions: isothermal and steady state conditions, constant longitudinal temperature, negligible pressure losses, perfect gas behavior, negligible radial temperature and concentration profiles (one dimensional model), negligible effect of competitive reactions, no isotope effects. In the model, the tubular catalytic membrane reactor is divided into finite volume elements where composition of the gas, rate of the reaction and hydrogen permeation through the walls can be considered constant (perfect mixing).

In terms of partial pressures for each chemical

species, in the generic finite element "i" the axial mass balance is for each gaseous specie:

$$P_i = (P_{i-1} v_{i-1} - c_s R T r_{i-1} dl - J_p) / v_i \quad (2)$$

where

r_i = reaction rate,

P_i = partial pressure,

c_s = stoichiometric coefficient for the water gas shift reaction; this is +1 for CO and H₂, -1 for CO₂ and H₂O, and 0 for the inert gas

dl = length of the finite element,

R = gas law constant,

T = temperature,

ε = catalyst void fraction

v_i is the gas velocity, given by:

$$v_i = v_{i-1} + \frac{RT}{P_{tot}} \frac{-AJ_p}{d_{in}(1-\varepsilon)} dl \quad (3)$$

P_{tot} = total pressure inside the reactor,

d_{in} = internal diameter,

J_p is the hydrogen permeation flux; it is considered to be controlled by three mass-transfer resistances:

- R_F is the resistance through the film at the interface between the inside membrane wall and the gas;

- R_C is the resistance through the ceramic support;

- R_M is the resistance through the Pd/Ag layer.

The fluxes through the film, the porous ceramic membrane and the metallic layer are respectively:

$$J_F = \frac{P_b - P_{int}}{R_F}; J_C = \frac{P_{int} - P_m}{R_C}; \quad (4)$$

$$J_M = \frac{\sqrt{P_m} - \sqrt{P_{strip}}}{R_M}$$

where

P_b = hydrogen pressure in the bulk gas;

P_{int} = hydrogen partial pressure at the gas/membrane interface;

P_m = hydrogen partial pressure at the ceramic Pd/Ag interface

P_{strip} = hydrogen pressure at the permeate side

R_F is evaluated by means of the Colburn analogy. R_C is evaluated by using the Knudsen diffusion theory.

The metallic film resistance is:

$$R_M = \delta_M / P_M \quad (5)$$

where δ_M and P_M are the thickness and the permeability of the Pd/Ag coating, respectively.

At the steady state the expression of the hydrogen permeation flux can be obtained by equating the hydrogen fluxes through the film the ceramic support and the metallic layer. The mass balance equation (2) is used for each of the reacting species.

Based on the model, the WGS code can be used to analyze the performances of a CMR, a conventional fixed bed reactor (posing $J_p=0$) and a permeator (posing $r_i=0$). Furthermore, with minor modifications concerning the reaction kinetic expression, the WGS code can be used for studying other hydrogenation/dehydrogenation reactions in a CMR.

The simulation code WGS has allowed us to verify that for the water gas shift reaction the conversion is not really modified by using a thin rolled Pd/Ag metallic membranes (50-70 μm) over a macro-porous ceramic tube instead of an electroless thin film (10 μm) coated on an asymmetrical ceramic tube with a dense top layer for the considered working temperature (350°C) [10]. As a matter of fact, the capability of the membrane and the CMR to separate and recover hydrogen can be evaluated by the reaction conversion:

$$\frac{H_2O_{fed} - H_2O_{reacted}}{H_2O_{fed}} \quad (6)$$

Figs. 5 and 6 show the partial pressure profiles of water and hydrogen inside the reactor operating at 0.2 MPa and 350°C with a stoich-

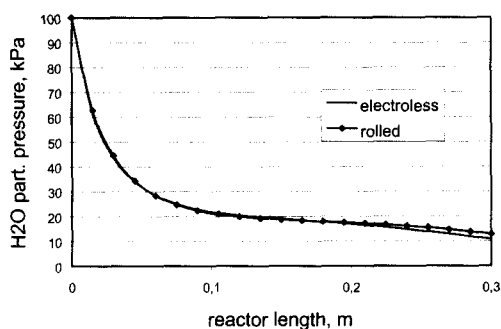


Fig. 5. Water partial pressure profile in a CMR with an electroless membrane.

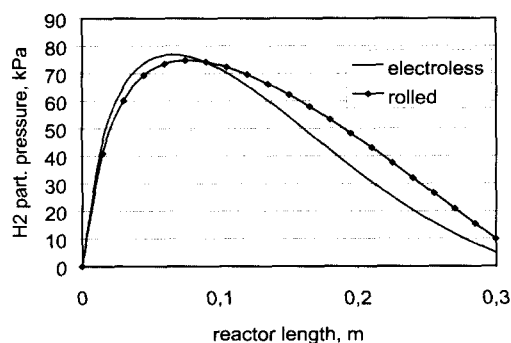


Fig. 6. Hydrogen partial pressure profile in a CMR with an electroless membrane.

ometric feed of CO and water. The water partial pressure calculated by the computer code at the reactor outlet is 8.08 and 8.78 kPa and the conversion is 95.6% and 95.2%, for the electroless and the rolled membrane respectively (the equilibrium conversion value under these operating conditions is about 82%). The difference in terms of the reactor performances is negligible; as matter of fact, the larger hydrogen mass transfer resistance of the rolled membrane (larger metal thickness) is compensated by the presence of a ceramic porous tube with a dense top layer in the electroless membrane.

4.2. Potential Application in the Fuel Cycle of a Fusion Reactor

The potential fuel cycle applications of Pd/Ag thin membrane permeators and of CMRs have

been also studied. A closed-loop process for the conversion of tritiated water into elemental hydrogen has been proposed with reference to the design requirements of the ITER blanket tritium recovery system [8,9]. The conversion of the tritiated water collected as impurity in the cryogenic traps is attained in a process characterized by a low processing rate, estimated in 1 mol/h. The main advantages are related to the absence of secondary wastes, low tritium inventories, moderate operating temperatures and pressures increasing both the reliability and safety of the nuclear plant.

In this process water is recovered in liquid form at the bottom of the cryogenics traps during the regeneration, which takes place by heating to ambient temperature. The liquid water collected at the bottom of the cryogenics traps is pumped into a stream of hot CO and routed to a CMR where the reaction (1) of tritiated water with CO to produce hydrogen isotopes and CO₂ is promoted. In a CMR the conversion of the reaction can be up to 99.8% since the equilibrium is displaced towards the products by the hydrogen extraction.

The CO used for the conversion is drawn from a vessel holding the amount required to process the whole batch of water plus a reasonable excess. The gas stream at the reactor outlet containing CO₂ produced by the reaction is recycled to the storage vessel. Therefore, the stream recycled to the CMR becomes progressively enriched in CO₂. Although, in these conditions, the reaction rate decreases, the reaction completion can be ensured by the recirculation of the reaction products. The process lasts until all the water is reacted and all the hydrogen isotopes are recovered by permeation.

When the conversion is completed, the CO₂ produced from the water gas shift reaction and the residual content of CO are discharged to the process waste detritiation for the removal of the residual tritium content. Alternatively, it is possible to reconvert the CO₂ into CO, to avoid the generation of CO₂ wastes and CO consumption. The mixture of CO₂ with the residual

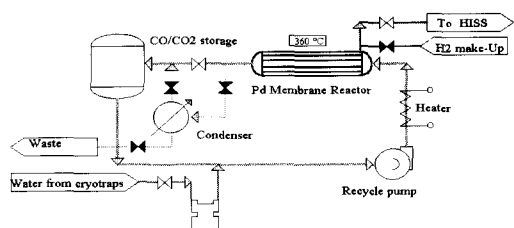


Fig. 7. Scheme of the closed-loop tritiated water conversion process.

amount of CO remaining in the storage vessel is added of hydrogen and sent to the CMR. By effect of the introduction of hydrogen, the water gas shift reaction (1) is reversed and the CO₂ is reconverted into CO:



The reaction is forced towards the complete conversion of CO₂ into CO by separating the formed water by means of a cryogenic trap. The dried gas stream is sent to the storage vessel and then back to the CMR. During this step it could be convenient to rise the temperature to reach thermodynamic equilibrium conditions, that are more favorable to the conversion of water. However, to avoid thermal cycling of the equipment, it is preferred to operate at constant temperature and to enhance the rate of conversion by increasing the rate of circulation of the gas through the CMR. A schematic flow sheet of the process is reported in Fig. 7.

The main feature of the process proposed is a reduced number of components, valves and controls. The CMR is a tubular reactor composed by a bundle of 40 tubes made of porous ceramic covered by a thin film of Pd/Ag. Tubes are 30 mm diameter and 1 m length, filled with Fe-Cr oxide catalyst. The CO/CO₂ storage vessel is a reservoir of 0.62 m³ volume operating at 1 bar abs during water conversion and at 1.6 bar abs during CO₂ regeneration. The water injection pump provides for the addition of tritiated water to the loop; the speed is adjustable

up to 0.072 l/h (4 mol/h). The recycle pump provides for gas circulation through the loop.

5. Experimental Results

Experimental tests have been carried out to characterize both the composite membranes and the catalytic membrane reactors.

Due to the presence of micro-holes on the metallic surface the electroless membranes have shown a not complete selectivity and a limited durability: a separation factor between hydrogen and nitrogen in the range 10 to 100 has been measured.

Measurements on pure Pd rolled membrane of 56 μm of thickness at 350 °C and 0.12 MPa of transmembrane differential pressure have exhibited a permeability value of $2.6 \times 10^{-10} \text{ m}^3/\text{m}^2 \text{ s Pa}^{0.5}$ with a complete hydrogen selectivity.

Tests for the water gas shift reaction on CMR with electroless membranes have shown that the reaction conversion is always above the equilibrium and increases when the flow rate decreases (the residence time increases). The effect of the membrane is very clear since the reaction is shifted towards the products because of the continuous hydrogen separation. The comparison between the experimental results

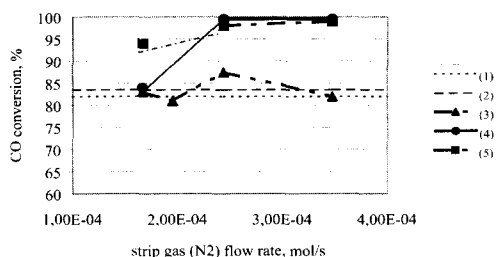


Fig. 8. CMR with rolled thin membrane, CO conversion vs. the N₂ strip flow rate: (1) equilibrium value at 350 °C, (2) equilibrium value at 331 °C, (3) co-current with feed flow rate $7.13 \times 10^{-4} \text{ mol/s}$ at 350 °C, (4) counter-current with feed flow rate $3.05 \times 10^{-3} \text{ mol/s}$ at 331 °C, (5) co-current with feed flow rate $3.05 \times 10^{-3} \text{ mol/s}$ at 331 °C.

and the model calculations shows an excellent accordance.

Tests on prototype CMR with Pd rolled thin membrane (70 μm thick) have been carried out, too. Fig. 8 shows the results obtained at 331°C (co-current and countercurrent mode) and 350°C (countercurrent mode) with the internal pressure of 1.1×10^5 Pa. The feed flow rate range is 3.05×10^{-5} mol/s and 7.13×10^{-4} mol/s with a stoichiometric $\text{H}_2\text{O}/\text{CO}$ composition. A nitrogen stream has been sent in the strip side at atmospheric pressure. The results have exhibited the reaction conversion arising up to 100% by increasing the nitrogen strip flow rate. Due to the catalyst characteristics, the reaction yield optimum is obtained at 330°C.

6. Conclusions

The PdAg layers of the electroless membranes are not flawless and chemically stable: as a consequence, these membrane have shown a not complete hydrogen selectivity and a limited durability. Nevertheless, these membranes have exhibited high hydrogen permeation fluxes and a significant separation factor between hydrogen and inert gas. Furthermore, according to the theoretical forecasts, the experimental tests have confirmed that the equilibrium shifts towards the dehydrogenation with a very high conversion. Thus, the CMR with electroless membranes is already applicable for some industrial processes, i.e. in the hydrocarbons hydrogenation or dehydrogenation.

Conversely, the rolled Pd and Pd/Ag membranes have separated hydrogen from the other gases

with a complete selectivity, thus showing a slightly larger mass transfer resistance with respect to thin film membranes. Experimental tests have confirmed the theoretical forecasts and the good performances over many weeks of operation. Thus, these rolled membranes are adequate for applications in the fusion reactor fuel cycle as well as in the industrial processes, where high pure hydrogen is required (i.e. hydrocarbon reforming for fuel cells).

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