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Pd–Ag membrane reactors for water gas shift reaction

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Abstract

Pd–Ag thin wall permeators have been obtained by coating ceramic porous tubes with thin Pd–Ag metal foils (50 μm). A procedure of cold rolling and annealing has been used for producing thin metal foils. These membranes and membrane reactors have been proposed to recover hydrogen (and its isotopes) from tritiated water by using the water gas shift reaction, and by the reverse reaction (CO_2 conversion) for applications in the fusion reactor fuel cycle.

The rolled membranes have been tested at 135–360 °C with a hydrogen transmembrane pressure in the range 130–180 kPa and hydrogen flow rates up to 1.02×10^{-4} mol s^{-1}. Both a complete hydrogen selectivity and a good chemical and physical stability have been observed through long-term tests. The tests on the membrane reactors have been carried out at the temperature of 325–330 °C with a feed pressure of 100 kPa; in particular, reaction conversion values close to 100% (well above the equilibrium value, about 80%) have been attained with the water gas shift reaction. These tests have demonstrated their applicability to the fusion fuel cycle as well as to the hydrogenation or dehydrogenation processes involving the use or the production of highly pure hydrogen.

Keywords: Pd–Ag membrane reactors; Water gas shift reaction; Hydrogenation and dehydrogenation processes; Tritiated water; Permeation; Permselectivity

1. Introduction

Palladium and palladium alloy membranes show very high performances in terms of hydrogen permeability because of the high solubility and diffusivity of the hydrogen and its isotopes in their lattice [1–5]. In particular, by adding silver to palladium, we can ensure a reduced metal embrittlement as well as a higher hydrogen permeability values, than pure palladium alone. Therefore, Pd–Ag alloys are used to prepare commercial permeator tubes of thickness 100–150 μm for hydrogen purification and separation.

For the past few years, interesting developments have been raised around the membrane reactors; they have been obtained by filling the lumen of these Pd–Ag membranes with a catalyst bed, where a dehydrogenation reaction is promoted: the gain in terms of hydrogen permeation turns into an increase in the reaction conversion (equilibrium shifting). In fact, the hydrogen produced in the dehydrogenation reactions permeates the membrane, and the reaction is moved towards the products beyond the thermodynamic equilibrium [6].

A general issue in the palladium membrane and membrane reactor technology is the achievement of high selectivity (or permselectivity) and high permeability [7–9]: both these properties contribute to reduce sizes and costs. Mainly, a complete hydrogen selectivity, besides the high permeability, is required for the palladium-based membranes used in applications with high pure hydrogen production. Examples of this procedure are found in nuclear processes, such as separation of hydrogen and its isotopes [10–13], and in recent energy applications, like pure hydrogen production by steam reforming of hydrocarbons [14–16]. Furthermore, the use of the membrane technologies has been proposed for applications in the fusion reactor fuel cycle. In this particular case, a mandatory requirement for the membranes to avoid any tritium loss, is the achievement of a complete hydrogen selectivity, in order to both reduce the number of process units and be able to operate in a continuous mode.

The development and creation of thin palladium membranes have been carried out to separate tritium (the mass-3 hydrogen isotope) from tritiated water by means of the water gas shift reaction [17]:

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad (1)$$

Furthermore, a “closed loop process”, based on a batch mode operation by one membrane reactor for both the water gas

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shift reaction (1) and the reverse reaction (CO_2 conversion):

$$CO_2 + H_2 \Leftrightarrow CO + H_2O \qquad (2)$$

has been proposed in order to avoid any production of tritiated wastes and consumption of CO with respect to the once through process [18].

The thermal, chemical and mechanical stability of the membranes is also a requirement for these applications. Among the production techniques of thin-film membranes, the electroless deposition of Pd–Ag thin layer (2.5–20 μm) on porous ceramic tubes was the first one to be realized in our group [19]. Nevertheless, these electroless membranes have shown the presence of micro-holes (no good permselectivity) and the metallic layer peeling under thermal and hydrogenation–dehydrogenation cycling. Finally, rolled membranes (50–70 μm) have been obtained by a procedure of cold rolling and annealing of metal foils [20]: these metal foils have then been joined by a diffusion bonding procedure in order to obtain permeator tubes.

The larger thickness in these rolled membranes, compared to the electroless ones, has ensured the absence of defects in the metal layer, and hence the complete hydrogen selectivity. Furthermore, the rolled membranes have shown high hydrogen permeability and durability. The membrane reactors have also exhibited conversion values suitable to the operating conditions relevant to the "closed loop process".

2. Rolled membranes

Pd–Ag sheets have been cold-rolled by a four-high mill with front and back tension. Several steps of cold rolling and annealing of Pd–Ag foils have been necessary in order to relieve the hardening due to the rolling.

The annealing of the metal foils has been carried out by a heat treatment in a furnace at 1200 °C for 2–3 h under Ar atmosphere (with 5% of H_2) at 100 kPa to avoid the oxidation and tarnishing of the palladium surfaces. After this initial process, the rolled thin foils (thickness in the range 50–70 μm) have been wrapped round and joined to obtain permeating tubes of length 150 mm and internal diameter 10 mm. To produce the permeator tubes, the Pd–Ag foils have been joined by diffusion bonding: this is a solid-state process in which the two surfaces to be joined are brought to high temperature by applying a controlled pressure [21,22].

This new technique [23], as an alternative to the inert gas tungsten arc welding previously used [20], has avoided the presence of thermal stressed zones along the permeator tubes where the formation of defects and cracks has occurred under operating conditions (thermal and hydrogenation cycling of the permeator tubes).

Tapes having a width of about 40 mm and thickness of 50 μm have been produced from the Pd–Ag rolled thin foils using the diffusion bonding procedure. These tapes have been cut in order to obtain slices fit to cover the tube surface with a mired width. The edges of the slice have been overlapped and joined by using a device where a controlled pressure is applied on the overlapped limbs of the Pd–Ag tube to be bonded.

The diffusion bonding process, due to the high mobility of the Ag atoms in the Pd–Ag alloy lattice, has been carried out in a furnace at 100 kPa under a reducing atmosphere (Ar with 5% of H_2).

The heat treatment consists in the following steps:

- heating up to a temperature of 720 °C at a ramp rate of 6 °C min^{-1},
- heating up to a temperature of 1100 °C at a ramp rate of 12 °C min^{-1},
- holding at 1100 °C for 1 h, and
- free cooling down to room temperature (in about 3 h).

Due to the high vapor pressure of the silver, no higher temperature nor vacuum have been applied during the heat treatment in order to avoid the silver evaporation, and thus the change in the Pd–Ag alloy composition.

3. Membrane modules

The Pd–Ag membrane (thickness 50–70 μm, diameter 10 mm and length 150 mm, permeation area 4.71×10^{-3} m^2)

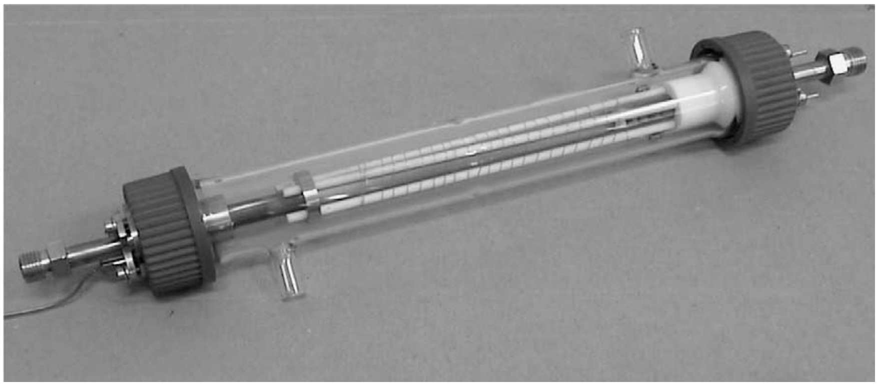

Fig. 1. The prototype membrane reactor.

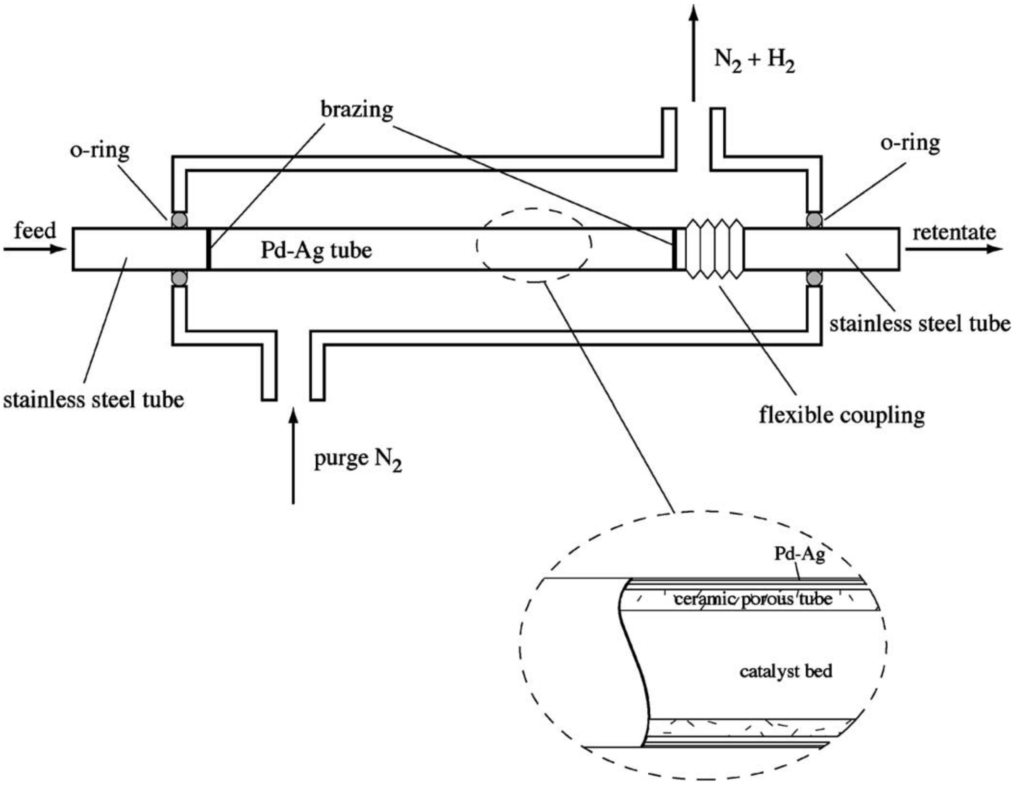

Fig. 2. Schematic view of the membrane reactor.

is joined and wrapped around a ceramic porous tube (internal/external diameter of 8/10 mm and pore size 10 μm) that has the function of avoiding both compression failures of the thin metal tube and the contact with the catalyst bed in the membrane reactor. The annular space between the metallic membrane and the ceramic porous tube is the minimum clearance (20–40 μm) required for easily inserting and moving the ceramic tube inside the metallic membrane. Particularly, this floating fit between the membrane tube and the ceramic support avoids the stresses at the metal–ceramic interface and ensure a good chemical and physical stability.

These Pd–Ag membranes have been encapsulated into a Pyrex module to capture the permeating gas and handle the retentate stream so that it is necessary to ensure the seal between the membrane and the rest of the module (or reactor unit). The hydrogen, permeated through the palladium membrane, is removed from the reactor shell by an inert gas stripping (in co-current or counter-current mode). The gas-tightness between the membrane tube and the Pyrex shell has been assured by o-rings inserted between the flanges and the membrane edges (see Fig. 1).

Two stainless steel tubes at both ends of the rolled tubular membranes, 10 mm diameter and 100 μm thick, have been brazed in order to have both low thermal conductance and mechanical stiffness (and hence low temperature and structural strength) in the o-ring zone of the membrane module under operating conditions. A flexible coupling has been added between the Pd–Ag and the steel tube in order to compensate the different thermal expansion of the membrane and the Pyrex shell module (see Fig. 2).

The membrane lumen is filled by a bed of low-temperature shift catalyst, type LK-821-2 (furnished by Haldor Topsoe, DK).

In reaction (1) mode, the reactants, H_2O and CO, are fed from the inlet side of the membrane through the catalyst bed. The hydrogen produced permeates the membrane and is recovered in the shell side of the reactor, while the CO_2 produced with the non-reacted water and CO and traces of H_2 are recovered at the outlet side of the tubular membrane. For the reverse reaction (2), CO_2 and H_2 are fed into the membrane lumen and the reactor shell is filled by H_2 at pressure of 125 kPa.

4. Experimental apparatus

A pilot plant has been realized for testing both the membranes and the membrane reactors under operating conditions simulating the closed loop process.

4.1. Closed loop process

In the fusion reactor fuel cycle, the tritium produced in the breeder blanket has to be recovered, purified and sent to the plasma chamber, where it would burn with deuterium to uphold the nuclear reaction. In the closed loop

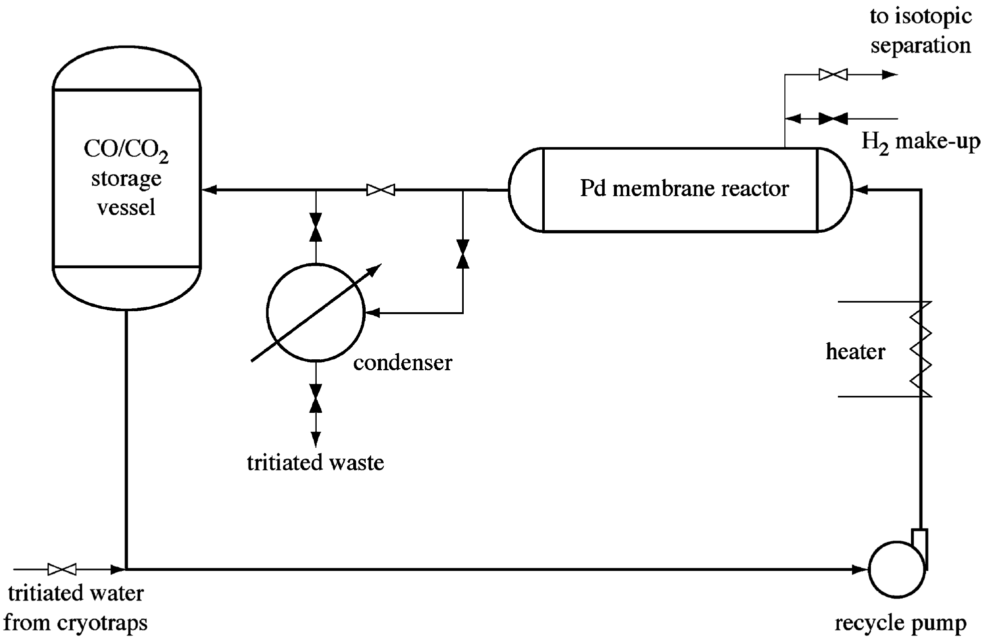

Fig. 3. Scheme of the closed loop process.

process, tritium in the form of tritiated water (HTO) coming from the breeding blanket is collected into cryogenic traps.

With respect to the once through process, where tritiated water is treated in a membrane reactor for the water gas shift reaction, this process has the main advantage of avoiding a large production of tritiated wastes (CO_2 plus non-reacted species) and the consumption of CO [18].

During the cryogenic traps regeneration of this closed loop process (see the schematic view in Fig. 3), the liquid water is pumped into a stream of hot CO by heating to ambient temperature and then it is routed to the membrane reactor where the reaction (1) of tritiated water with CO is promoted to produce hydrogen isotopes and CO_2. Accordingly to theoretical analyses and experimental results [18], the conversion of the reaction in a membrane reactor can be up to 99%, since the equilibrium is displaced towards the products by the hydrogen extraction. The pure hydrogen isotopes, recovered on the permeate side of the membrane reactor, are then directly sent to the isotopic separation system.

The CO required 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 CO_2 product from the reaction, is recycled to the storage vessel. Therefore, the stream recycled to the membrane reactor becomes progressively enriched in CO_2. Although the reaction conversion is decreased in these conditions, the completion of the reaction can be ensured by the re-circulation of the reaction products. The process lasts until all of the water reacts and all the hydrogen isotopes are recovered by permeation.

When the conversion is completed, the mixture of CO_2 with the residual amount of CO remaining in the storage vessel is added of hydrogen and sent to the membrane reactor. By effect of the hydrogen introduction, the water gas shift reaction (1) is reversed and the CO_2 is reconverted into CO by reaction (2).

The reaction is forced towards the complete conversion of CO_2 into CO by separating the water formed by means of a condenser. The dried gas stream is sent to the storage vessel and then back to the membrane reactor. During this step, it could be convenient to increase the temperature: as matter of fact, from thermodynamic considerations, the conversion reaction is promoted by increasing the temperature (the behavior of the equilibrium constant vs. the temperature is inverted with respect to the water gas shift). However, to avoid thermal cycling of the equipment, it is preferred to operate at constant temperature and to enhance the conversion rate by increasing the circulation rate of the gas through the membrane reactor.

4.2. Pilot plant

A pilot plant has been realized for testing the membranes and membrane reactors. The main components of the plant are:

- a micro-pump (ISMATEC-SA) for the injection of controlled quantities of distilled water,
- an electrically heated mixer that allows for the evaporation of water in the gas stream,
- four bottles for the supply of CO, CO_2, H_2 and inert gas (nitrogen); the flow rate of each stream is regulated by a mass flow controller,

- a water trap, and
- a gas chromatograph for analyzing the composition of the gases coming from the membrane reactor (CO, CO_2 and possibly methane and other hydrocarbons produced by competitive reactions).

The reactor is equipped with an electrical heater (Pt winding) to maintain the operating temperature over 300 °C in order both to optimize the reaction kinetics and avoid the CO poisoning of the Pd–Ag metallic layer. A thermocouple is located along the membrane axis to control that the reactor axial temperature profile stays almost flat, by avoiding non-isothermal working conditions.

For direct reaction (1), liquid water and CO are fed to an electrically heated mixer, where water is evaporated, and then to the membrane reactor where the reaction above 300 °C, produces H_2 and CO_2. The hydrogen formed permeates through the Pd–Ag membrane into the shell side, and is displaced by a purge of inert gas.

The H_2 and inert gas mixture at the outlet of the reactor shell is analyzed, while the CO_2, H_2O and other gases coming from the membrane reactor are analyzed by a gas chromatograph (GC). Prior to reaching the GC, the mixture is purified from its residual water content by means of a dryer, consisting in a bottle filled with silica gel in order to protect the GC column. The bottle can be weighed to evaluate the amount of water produced.

To test the reverse reaction (2), H_2 and CO_2 are fed into the membrane reactor under a controlled flow rate. The mixture enters the membrane reactor, where the reaction at temperature of 330 °C produces H_2O and CO.

The products coming from the membrane reactor are dehydrated in the water trap and then are analyzed by the GC. In Fig. 4, the scheme of the proposed pilot plant (with measurement and control instruments) is reported.

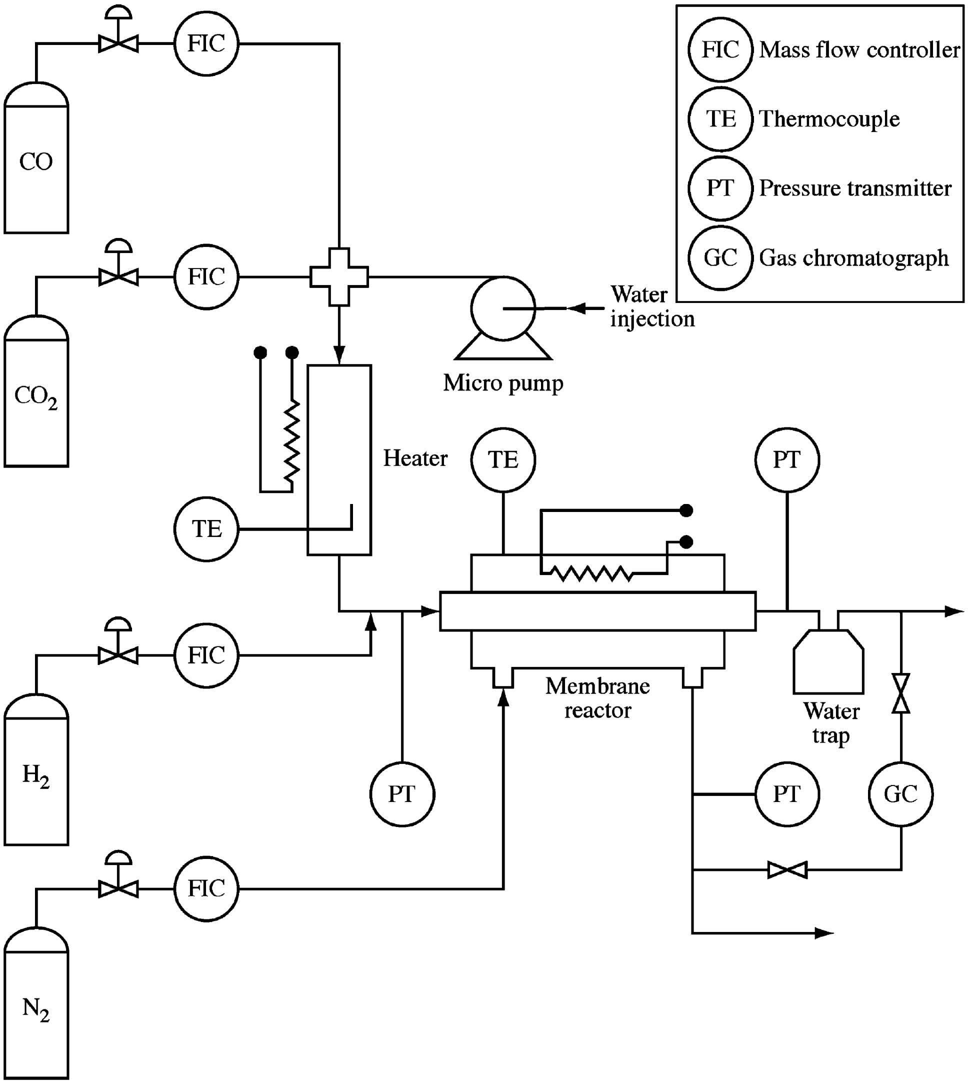

Fig. 4. Scheme of the pilot plant.

5. Experimental results

The membrane modules have first been tested with a controlled hydrogen flux in order to evaluate the permeability of the Pd–Ag tubes. Then, reaction tests for both the water gas shift reaction (1) and the CO_2 conversion (2) have been carried out.

5.1. Membranes testing

In these tests, Pd–Ag rolled membranes have been characterized by measuring the hydrogen permeated flux under a controlled transmembrane differential pressure. The gas flux through the composite membrane depends on the mass transfer resistances through the gaseous film, the ceramic support and the metal layer. The controlling mass transfer mechanism is the permeation through the metal layer (Sievert law) and the permeance is measured in $\mathrm{mol\,m^{-2}\,s^{-1}\,Pa^{-0.5}}$ (as an example, at 300 °C for a Pd–Ag rolled membrane of thickness 50 μm supported on a ceramic tube of internal/external diameter 8/10 mm and pore size of 10 μm, the calculated contribution of the metal to the total mass transfer resistance is about 80%).

A rolled membrane, thickness 68 μm, obtained by eight steps of rolling and annealing, has been tested for 6 months. The membrane has been operated with a feed hydrogen pressure in the range 130–180 kPa and at atmospheric pressure in the shell side (without purging).

On the ground of the experimental data, the following formulas for the hydrogen permeance have been obtained in two different temperature ranges:

$$P = 7.2 \times 10^{-4}\, e^{-1866.6/T\,(\mathrm{K})}\ \mathrm{mol\,m^{-2}\,s^{-1}\,Pa^{-0.5}}$$

for $T = 135$–$275\,^{\circ}\mathrm{C}$

and

$$P = 5.8 \times 10^{-5}\, e^{-521.0/T\,(\mathrm{K})}\ \mathrm{mol\,m^{-2}\,s^{-1}\,Pa^{-0.5}}$$

for $T = 276$–$360\,^{\circ}\mathrm{C}$

These results are in agreements with the literature data [24] (see Fig. 5).

5.2. Membrane reactors testing

After the membrane testing, the membrane reactor has been tested in the pilot plant (see Section 4) in order to verify the performances in terms of both reaction conversion and durability in long-term tests.

5.2.1. Water gas shift reaction

The tests carried out during several months of operation have simulated the water gas shift reaction. The operating conditions have been:

- temperature of 325 °C,
- feed pressure of 100 kPa,
- shell pressure of 100 kPa, and
- nitrogen (purging gas) flow rate of $2.74 \times 10^{-4}\ \mathrm{mol\,s^{-1}}$.

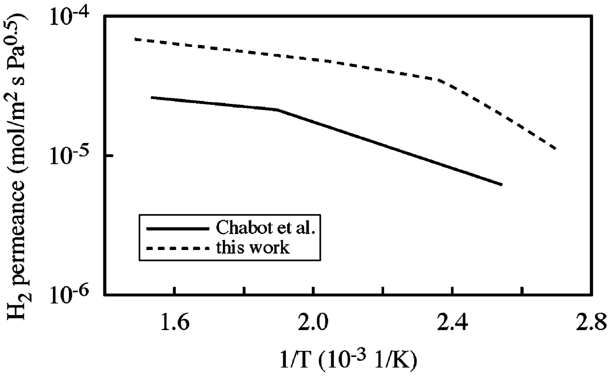

Fig. 5. Measured hydrogen permeance.

Table 1
Water gas shift reaction conversion values

CO feed flow rate ($\mathrm{mol\,s^{-1}}$)	Reaction conversion (%)	H_2 permeated (%)
1.95×10^{-5}	98.2	83.0
4.77×10^{-5}	97.7	44.2
9.03×10^{-5}	96.6	17.6

The results described below show conversion values >95% (well above the thermodynamic equilibrium): the capability of the membrane to remove the hydrogen produced and to shift the equilibrium is well evident.

5.2.1.1. Case 1—feed composition: $CO = H_2O = 0.5$. The CO feed flow rate has ranged from 1.95×10^{-5} to $9.03 \times 10^{-5}\ \mathrm{mol\,s^{-1}}$; the reaction conversion values (calculated as the percentage of CO reacted on CO fed) have been found to be in the range from 96.6 to 98.2%, as reported in Table 1.

5.2.1.2. Case 2—feed composition: $CO = 0.4$ and $H_2O = 0.6$. In these tests, an excess of water has been used (feed molar ratio $H_2O/CO = 1.5$); operating with the CO feed flow rate from 1.95×10^{-5} to $9.03 \times 10^{-5}\ \mathrm{mol\,s^{-1}}$ reaction conversion values have been found to be in the range from 97.8 to 98.9%, as reported in Table 2.

The results of the cases 1 and 2 show that the reaction conversion increases by reducing the feed flow rate (i.e. increasing the residence time), and an excess of water in the

Table 2
Water gas shift reaction conversion values

CO feed flow rate ($\mathrm{mol\,s^{-1}}$)	Reaction conversion (%)	H_2 permeated (%)
1.95×10^{-5}	98.9	70.6
4.77×10^{-5}	98.0	24.0
9.03×10^{-5}	97.8	14.0

Table 3
Water gas shift reaction conversion values

CO feed flow rate (mol s^{-1})	Reaction conversion (%)	H_2 permeated (%)
1.95×10^{-5}	96.5	28.9
4.77×10^{-5}	96.6	10.2
6.02×10^{-5}	96.0	8.10
9.03×10^{-5}	95.4	4.90

feed stream (case 2) produces an increase in the conversion. Both behaviors have been observed and reported in literature: Uemiya et al. [6] have operated at 400 °C a palladium membrane reactor for the water gas shift reaction obtaining comparable conversion values.

5.2.1.3. Case 3—feed composition: CO = 0.2, H_2O = 0.3 and CO_2 = 0.5. In these tests, a feed molar ratio of $H_2O/CO = 1.5$ has been used and CO_2 has been added to the feed stream in order to simulate a different phase in the closed loop process. The CO feed flow rate has ranged from 1.95×10^{-5} to 9.03×10^{-5} mol s^{-1}. With respect to the previous cases, the addition of CO_2 reduces the reaction conversion (values in the range from 95.4 to 96.6%) (see Table 3).

These results show that at low surface velocity values (feed composition $CO = H_2O = 0.5$ and CO feed flow rate of 1.95×10^{-5} mol s^{-1}), a large amount of the hydrogen produced from the shift reaction permeates through the membrane and is collected in the shell side; at higher surface velocity values, the percentage of permeated hydrogen decreases (see Fig. 6). Nevertheless, reaction conversion values very close to the complete conversion have been found in all the previous cases.

5.2.1.4. Case 4. In this set of tests, the feed composition has been varied by maintaining constant the residence time (total feed flow rate at 9.75×10^{-5} mol s^{-1}). The results are reported in Table 4.

The use of CO_2 ($CO = 0.2$, $H_2O = 0.3$ and $CO_2 = 0.5$) in the feed stream reduces the hydrogen partial pressure (i.e. the permeation driving force), thus reducing both the reaction conversion (the excess of CO_2 promotes the reverse reaction) and the hydrogen permeated. It is clear that the highest reaction conversion is obtained when a feed flow rate with an excess of water is used ($CO = 0.4$ and $H_2O = 0.6$) and a higher amount of the hydrogen is permeated (effect of the membrane on the equilibrium shift).

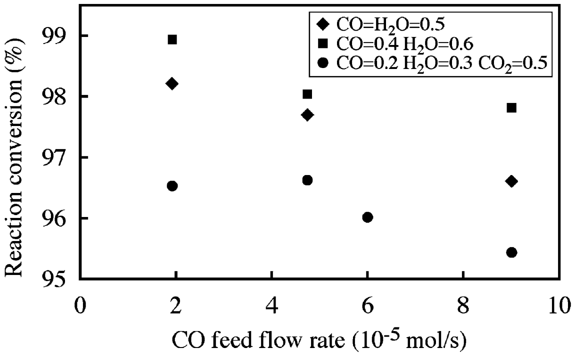

Fig. 6. Measured conversion values for the water gas shift reaction.

5.2.1.5. Case 5. As in the previous case, an analysis has been carried out by varying the feed composition. This time, a higher total feed flow rate (2.38×10^{-4} mol s^{-1}) has been used instead. The results are reported in Table 5.

In comparison to the previous case, the higher feed flow rate reduces the residence time and the hydrogen mass transfer through the membrane: in fact, a reduced amount of permeated hydrogen is observed. Nevertheless, this fact does not significantly affect the reaction conversion and the higher values are observed for the case $CO = 0.4$ and $H_2O = 0.6$.

5.2.2. CO_2 Conversion

In order to verify the effectiveness of the use of the membrane reactor in the “closed loop process”, tests simulating the CO_2 conversion (the reverse reaction with respect to the water gas shift) have been carried out. A feed molar composition ($H_2 = CO_2 = 0.5$) has been fed into the membrane lumen at 100 kPa and at 325–330 °C (see Table 6).

Table 4
Water gas shift reaction conversion values

CO feed flow rate (mol s^{-1})	Reaction conversion (%)	H_2 permeated (%)	Feed composition
1.95×10^{-5}	96.5	28.9	$CO = 0.2$, $H_2O = 0.3$ and $CO_2 = 0.5$
3.90×10^{-5}	98.9	43.0	$CO = 0.4$ and $H_2O = 0.6$
4.87×10^{-5}	96.2	36.6	$CO = H_2O = 0.5$

Table 5
Water gas shift reaction conversion values

CO feed flow rate (mol s^{-1})	Reaction conversion (%)	H_2 permeated (%)	Feed composition
4.77×10^{-5}	96.6	10.2	$CO = 0.2$, $H_2O = 0.3$ and $CO_2 = 0.5$
9.53×10^{-5}	98.3	20	$CO = 0.4$ and $H_2O = 0.6$
1.19×10^{-4}	96.0	14.7	$CO = H_2O = 0.5$

Table 6
Water gas shift reverse reaction conversion values

CO_2 feed flow rate (mol s^{-1})	Reaction conversion (%)	
	Measured	Calculated
1.95×10^{-5}	15.2	16.7
4.77×10^{-5}	4.2	6.1
9.03×10^{-5}	3.1	3.4

For the CO_2 conversion, low values have been found accordingly with a simulation analysis carried out by a computer code based on a finite volume method applied to the membrane reactor [17]. This behavior can be explained by the fact that the thermodynamic equilibrium of reaction (2) is promoted by the temperature increase. As described for the "closed loop process" this reaction can be carried out by operating the membrane reactor at higher temperature or alternatively by using a higher re-circulation rate.

6. Conclusions

The Pd–Ag rolled sheets have been jointed by a new welding procedure. This new technique, alternative to the inert gas tungsten arc welding previously used, has avoided the formation of thermal stressed zones along the permeator tubes. In the new rolled membranes, the chemical and physical stability observed can be considered as a consequence of the fact that the diffusion bonding does not involve melting and microstructural degradation of the material.

The main advantages of the diffusion bonding process applied to the Pd–Ag tubes are:

- the welding is defect-free (absence of micro-holes), thus ensuring to the permeator tubes a complete hydrogen selectivity,
- heat affected zones are avoided so that the embrittlement of the Pd–Ag alloy under thermal and hydrogenation cycling is reduced.

These characteristics have been verified in long-term tests, where prototype membrane modules and catalytic membrane reactors for hydrogen selective separation and production via gas shift have been characterized.

Particularly, the long-term tests have been carried out to characterize both the membranes (permeability tests) and the membrane reactors (water gas shift and CO_2 conversion reaction tests). The reactor tests have been operated with reference to a "closed loop process" studied for application in the fusion fuel cycle. Mainly, with respect to a conventional reactor for the water gas shift reaction these membrane reactors have the capability to achieve high conversion values operating with low H_2O/CO ratios: this fact is very important in fusion nuclear applications where the tritium inventory can be reduced.

During several months, the membrane devices have been continuously operated and have showed complete hydrogen selectivity, high hydrogen permeability and reaction conversion values very close to 100%, thus demonstrating the effectiveness of the "membrane reactor" concept to applications for hydrogenation/dehydrogenation reactions. In fact, these characteristics make these rolled membranes suitable for applications in other energetic fields. Particularly, the costs reduction coming from the reduced amount of precious materials employed (metal thickness $<50\,\mu m$) and the development of cheap production technologies (diffusion welding) could demonstrate the viability of these membranes for the application in fuel cells systems where hydrogen, produced from hydrocarbon reforming, has to be separated from gases mixtures. As an example, thanks to the complete hydrogen selectivity, these membranes can be employed to produce ultra-pure hydrogen for polymeric fuel cells (characterized by high efficiency and low operating temperature) which are poisoned by very small amount of other gases (<10 ppm of CO).

As future work, in order to further reduce the costs, studies aimed both to reduce the membrane thickness as well as to use materials alternative to the Pd–Ag will be carried out.

References

[1] J. Shu, et al., Can. J. Chem. Eng. 69 (1991) 1036–1060.
[2] V. Gryaznov, Catal. Today 51 (1999) 391–395.
[3] J. Coronas, J. Santamaria, Catal. Today 51 (1999) 377–389.
[4] K.K. Sirkar, et al., Ind. Chem. Eng. Res. 38 (1999) 3715–3727.
[5] E. Drioli, et al., Clean Products Process. 2 (2000) 179–186.
[6] S. Uemiya, et al., Ind. Eng. Chem. Res. 30 (1991) 585–589.
[7] J.N. Armor, J. Membr. Sci. 147 (1998) 217–233.
[8] G. Saracco, et al., Chem. Eng. Sci. 54 (1999) 1997–2017.
[9] S. Uemiya, Separation Purification Meth. 28 (1) (1999) 51–85.
[10] H. Yoshida, et al., Nucl. Technol. Fus. 3 (1983) 471–484.
[11] R.D. Penzhorn, et al., Fus. Technol. 14 (1988) 450–455.
[12] V. Violante, et al., J. Membr. Sci. 104 (1995) 11–17.
[13] A. Basile, et al., Catal. Today 25 (1995) 321–326.
[14] K. Aasberg-Petersen, et al., Catal. Today 46 (1998) 193–201.
[15] J.C. Amphlett, et al., Int. J. Hydrogen Energy 21 (8) (1996) 673–678.
[16] E. Kikuchi, Catal. Today 56 (2000) 97–101.
[17] V. Violante, et al., Proceedings of the 19th SOFT, September 16–20, Lisbon, Fus. Technol. 2 (1996) 1205–1208.
[18] S. Tosti, et al., Proceedings of the 20th SOFT, September 7–11, Marseilles, Fus. Technol. 2 (1998) 1033–1036.
[19] S. Castelli, et al., Proceedings of the 20th SOFT, September 7–11, Marseilles, Fus. Technol. 2 (1998) 993–996.
[20] S. Tosti, et al., Int. J. Hydrogen Energy 25 (2000) 319–325.
[21] H. Guo, et al., Welding in the World 37 (3) (1996) 107–113.
[22] M.F. Islam, N. Ridley, Scripta Materialia 38 (8) (1998) 1187–1193.
[23] S. Tosti, et al., Diffusion bonding of Pd–Ag rolled membranes, Mater. Process. Technol., submitted for publication.
[24] J. Chabot, et al., Fus. Technol. 14 (1988) 614–618.