

Chapter 2

Pd-based Selective Membrane State-of-the-Art

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Abbreviations

AASR	Acetic acid steam reforming
BESR	Bioethanol steam reforming
CVD	Chemical vapour deposition
ELP	Electroless plating deposition
EP	Electroplating
ESR	Ethanol steam reforming
EVD	Electrochemical vapour deposition
FBR	Fixed bed reactor
GSR	Glycerol steam reforming
HTR	High temperature reactor
IUPAC	International Union of Pure and Applied Chemistry
LTR	Low temperature reactor
ML	Molecular layering
MR	Membrane reactor
MS	Magnetron sputtering
MSR	Methane steam reforming
PEMFC	Proton exchange membrane fuel cell
POM	Partial oxidation of methane
PSA	Pressure swing adsorption
PVD	Physical vapour deposition
SRM	Methanol steam reforming

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WGS	Water gas shift
WHSV	Weight hourly space velocity

List of Symbols

D	Diffusion coefficient
d_p	Pore diameter
E_a	Apparent activation energy
G	Geometrical factor
J	Flux or permeation rate
$J_{H_2, \text{Sieverts-Fick}}$	Hydrogen flux through the membrane according to Sieverts–Fick law
J_{H_2}	Hydrogen flux through the membrane
J_i	Flux of the i -species across the membrane
J_m	Mass flux
M_i	Molecular weight of the i -species
n	Dependence factor of the hydrogen flux on the hydrogen partial pressure
p	Pressure
$Pe_{H_2}^0$	The pre-exponential factor
Pe_{H_2}	The hydrogen permeability
$p_{H_2, \text{perm}}$	Hydrogen partial pressures at the permeate side
$p_{H_2, \text{ret}}$	Hydrogen partial pressures at the retentate side
R	Universal gas constant
T	Absolute temperature
X	Coordinate perpendicular to the transport barrier
$\Delta H_{298\text{ K}}^\circ$	Enthalpy variation in standard conditions
Δp_i	Pressure difference of species
α	Ideal separation factor or selectivity
δ	Membrane thickness
ϕ_{pore}	Pore diameter

2.1 Introduction

The first scientific study on palladium-based membranes, available in the Elsevier Scopus database [1], where more than 6,000 scientific journals are taken into account, is dated 1955, when Juenker et al. [2] analyzed the use of palladium membranes for hydrogen purification. Today, it is well known that the palladium membranes are, mainly, applied in the field of gas separation and, particularly, in the issue of the hydrogen rich-stream purification [3]. As reflected by the data of Fig. 2.1, the scientific interest towards palladium-based membranes is increased

Fig. 2.1 Number of published papers per year on palladium membrane applications

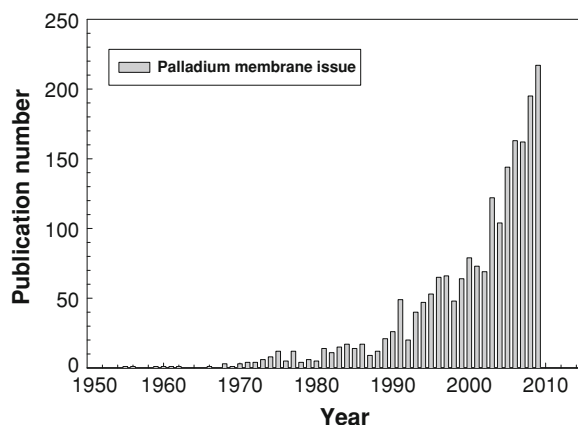
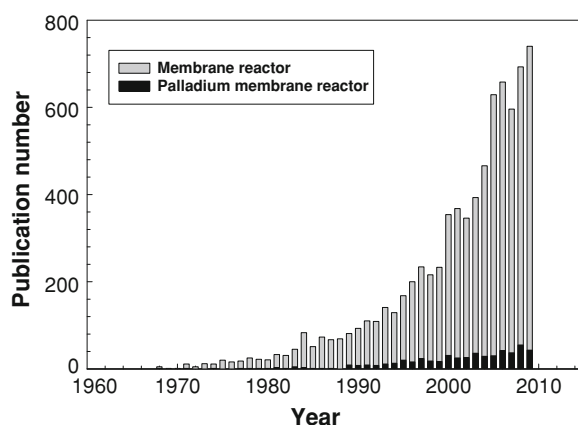


Fig. 2.2 Number of publications per year on membrane reactors area and on restricted area on palladium-based membrane reactors



especially in the last two decades. The statistics on the scientific publications in the contest of palladium membranes applications reported in the figure were made by means of Elsevier Scopus database.

Moreover, Fig. 2.2 points out further statistics data on palladium membranes applied in the field of membrane reactors (MRs), devices combining the separation properties of the membranes with the typical characteristics of catalytic reaction steps in only one unit. In particular, this figure reports the number of publications on palladium-based membranes reactors with respect to the total number of publications in the membrane reactors area.

The progress in the field of palladium-based MRs is due to their capacity to produce a pure hydrogen stream, owing to infinite hydrogen perm-selectivity with respect to all other gases. Moreover, in the last years the “hydrogen economy” has taken place in order to solve the problematic concerning the climate change and air pollution due to the emissions caused by the use of fossil fuels [4]. In particular, the “hydrogen economy” has been developed with the aim of using hydrogen as

an energy carrier, producible from renewable sources as an alternative to fossil fuels.

Nevertheless, the commercialization of pure palladium membranes is still limited by several factors:

- pure palladium membranes undergo the embrittlement phenomenon when exposed to pure hydrogen at temperatures below 300°C,
- pure palladium membranes are subject to deactivation by carbon compounds at temperature above 450°C,
- pure palladium membranes are subject to irreversible poisoning by sulphur compounds,
- the cost of palladium is high.

In order to reduce the aforementioned drawbacks, palladium can be alloyed with a variety of other metals in order to manufacture membranes able to increase the hydrogen permeability shown by the pure palladium membranes.

As a main scope, the present chapter will give an overview on the general classification of the membranes, paying particular attention to the palladium-based membranes and their applications, pointing out the most important benefits and the drawbacks due to their use. Finally, the application of palladium-based membranes in the area of the membrane reactors will be illustrated and such reaction processes in the issue of hydrogen production will be discussed.

2.2 Membrane Classification

As indicated by IUPAC definition [5], a *membrane* can be described as a structure having lateral dimensions much greater than its thickness through which mass transfer may occur under a variety of driving forces such as gradient of concentration, pressure, temperature, electric potential, etc. A schematic representation of a two-phase system separated by a membrane is given in Fig. 2.3, where the Phase 1 is usually considered as the feed, while the Phase 2 as the permeate.

As schematically resumed in Fig. 2.4, the membranes are classified on the base of their nature, geometry and separation regime [6].

The classification based on the membrane nature distinguishes them into biological and synthetic ones, differing completely for functionality and structure [7].

Biological membranes are easy to be manufactured, but they present many drawbacks such as limited operating temperature (below 100°C) and pH range, problems related to the clean-up and susceptibility to microbial attack due to their natural origin [7].

Synthetic membranes can be subdivided into organic (polymeric) and inorganic (ceramic, metallic) ones according to their operative temperature limit: *polymeric membranes* commonly operate between 100 and 300°C [8], above 200°C the *inorganic ones*.

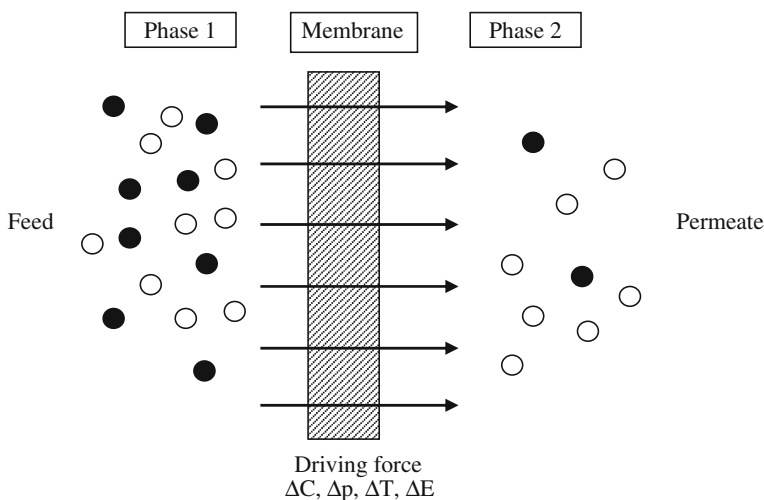


Fig. 2.3 Schematic representation of a two-phase system separated by a membrane

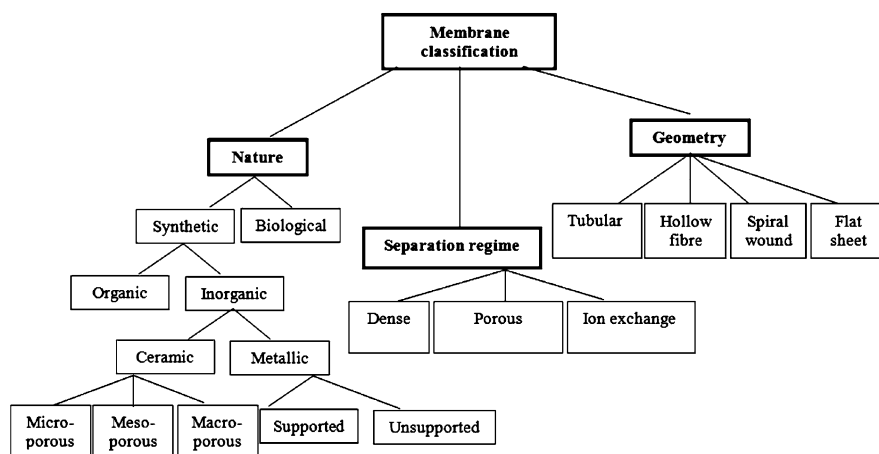


Fig. 2.4 Scheme of a general classification of the membranes

In the viewpoint of the morphology and/or membrane structure categorization, the inorganic membranes can be also subdivided into ceramics and metallic. In particular, *ceramics membranes* differ according to their pore diameter in microporous ($d_p < 2$ nm), mesoporous ($2 \text{ nm} < d_p < 50$ nm) and macroporous ($d_p > 50$ nm) [5]. Finally, *metallic membranes* can be categorized into supported and unsupported.

Generally, inorganic membranes are stable between 200 and 800°C and in some cases they can operate at elevated temperatures (ceramic membranes over 1000°C) [9].

Depending on their geometry, the membranes can be subdivided in *tubular*, *hollow fibre*, *spiral wound* and *flat sheet* [10]:

- *Tubular membranes* are easy to clean and show good hydrodynamic control, but as important drawbacks they require relatively high volume per membrane area unit and present high costs.
- *Hollow fibre membranes* can be considered as practical and cheaper alternatives than conventional chemical and physical separation processes. They offer high packing densities and they can withstand relatively high pressure owing to their structural integrity. In this contest, they allow flexibility in system design and operation.
- *Spiral wound membranes* offer advantages such as compactness, good membrane surface/volume and low capital/operating cost ratios. Nevertheless, they are not suitable for viscous fluid and are difficult to clean.
- *Flat sheet membranes* offer moderate membrane surface/volume ratios. However, they are susceptible to plugging due to flow stagnation points, difficult to clean and expensive.

A further membrane classification is based on the separation mechanism. There are three separation mechanisms depending on specific properties of the components [11]:

1. separation based on molecules/membrane surface interactions (e.g., multi-layer diffusion) and/or difference between the average pore diameter and the average free path of fluid molecules (e.g. *Knudsen mechanism*);
2. separation based on the difference of diffusivity and solubility of substances in the membrane: *solution/diffusion mechanism*;
3. separation due to the difference in charge of the species to be separated: *electrochemical effect*.

Based on these mechanisms, the membranes can be further classified in *porous*, *dense* and *ion-exchange*. In Table 2.1, the different diffusion mechanisms for porous and dense membranes are reported.

In the case of porous membranes:

- *Poiseuille (viscous flow) mechanism* occurs when the average pore diameter is bigger than the average free path of fluid molecules. In this case, the collisions among the different molecules are more frequent than those among the molecules and the porous wall: as a consequence no separation takes place [12].

Table 2.1 Diffusion mechanisms in porous and dense membranes

Membrane	d_{pore} (nm)	Diffusion mechanism
Macroporous	>50	Poiseuille (Viscous flow)
Mesoporous	2–50	Knudsen
Microporous	<2	Activated process
Dense Pd	–	Fick

- *Knudsen mechanism* occurs when the average pore diameter is similar to the average free path of fluid molecules. In this case, the collisions of the molecules with the porous wall are very frequent and the flux of the component permeating through the membrane is calculated by means of the following equation [12]:

$$J_i = \frac{G}{\sqrt{2 \cdot M_i \cdot R \cdot T}} \cdot \frac{\Delta p_i}{\delta} \quad (2.1)$$

where J_i is the flux of the i -species across the membrane, G the geometrical factor, which takes into account the membrane porosity and the pore tortuosity, M_i molecular weight of the i -species, R universal gas constant, T absolute temperature, Δp_i pressure difference of species and δ membrane thickness.

- *Surface diffusion* is achieved when one of the permeating molecules is adsorbed on the pore wall due to the active sites present in the membrane [13]. This type of mechanism can reduce the effective pore dimensions, unfavouring the transfer of different molecular species [14]. However, this diffusion can take place also in the presence of a Knudsen transport. This mechanism is less significant by increasing the temperature owing to the progressive decrease of the bond strength between molecules and surface.
- *Capillary condensation* occurs when one of the components condenses within the pores due to capillary forces, which are sufficiently strong only at low temperature and in presence of small pores. If the pores dimension is small and homogeneous and the pores are uniformly distributed on the membrane, this mechanism can offer high selectivity [15, 16]. Generally, the capillary condensation favours the transfer of relatively large molecules [17].
- *Multi-layer diffusion* is developed when the molecule/surface interactions are strong. This mechanism is like to an intermediate flow regime between surface diffusion and capillary condensation [18].
- *Molecular sieve* takes place when the pore diameters are very small, allowing the permeation of only smaller molecules.

In the case of dense membranes, the transport mechanism is a *solution-diffusion* mechanism, in which the dissociated molecules on the gas/membrane interface are adsorbed at the atomic level on the membrane surface. The atoms diffuse through the membrane and are re-combined to form molecules at the gas/membrane interface. Afterwards, they desorb.

Among all types of membranes, the inorganic dense membranes have attracted the interest of many researchers due to their capacity to separate completely a product from gaseous mixtures [19]. In particular, the dense palladium membranes are used because of their complete hydrogen perm-selectivity. In the last years, the increasing interest towards this type of membranes is, also, due to hydrogen application as energy carrier.

For this reason, in the following, a general introduction to pure palladium membranes is given.

2.3 Hydrogen Production and Palladium Membranes

In the current fossil fuel economy, the fossil fuels burning causes the emission of greenhouse gases and other pollutants. In order to mitigate the air pollution and the climate change, the use of alternative technologies is become necessary. In this contest, great interest is paid to PEMFCs, which are capable to produce electricity directly from hydrogen and oxygen, without combustion, making the process non-polluting [20]. A PEMFC uses a permeable polymeric membrane as the electrolyte (Fig. 2.5).

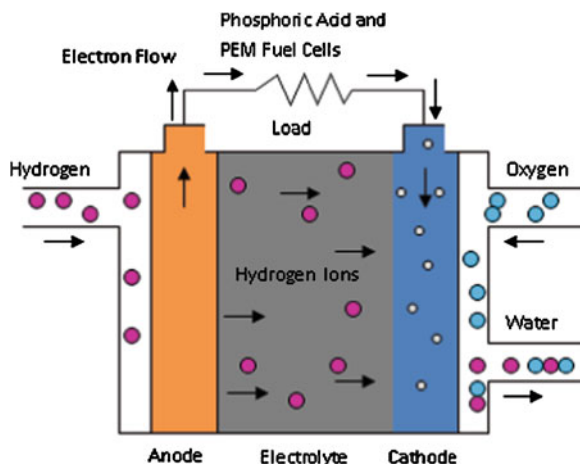
PEMFCs are characterized by low operative temperature (80–100°C), high current density, compactness, fast start-up and suitability for discontinuous operation [21]. These features make PEMFCs the most promising and attractive candidate for a wide variety of power applications ranging from portable/micropower and transport to large-scale stationary power systems for buildings and distributed generation [22], as shown in Fig. 2.6.

Today, the hydrogen for supplying the PEMFCs derives, mainly, from fossil fuels (48% from natural gas, 30% from oil and 18% from coal) [24]. Nevertheless, owing to the climate change as well as the cost increase of oil and gas, the development of a strategy for exploiting alternative and renewable sources represent a top priority in which hydrogen could be an inexhaustible energy carrier [25].

Nevertheless, the full commercialization of PEMFC systems needs a stable supply of hydrogen, which must be characterized by high purity for avoiding the CO poisoning of the PEMFC anodic catalyst [26].

Nowadays, the dominant technology for direct hydrogen production is steam reforming from hydrocarbons. Generally, reforming reactions, carried out in conventional fixed bed reactors (FBRs), produce a hydrogen rich gas mixture containing carbon oxides and other by-products as well as the unreacted reactants. Therefore, in the viewpoint of feeding a PEMFC, which can tolerate only

Fig. 2.5 Diagram of a PEM fuel cell



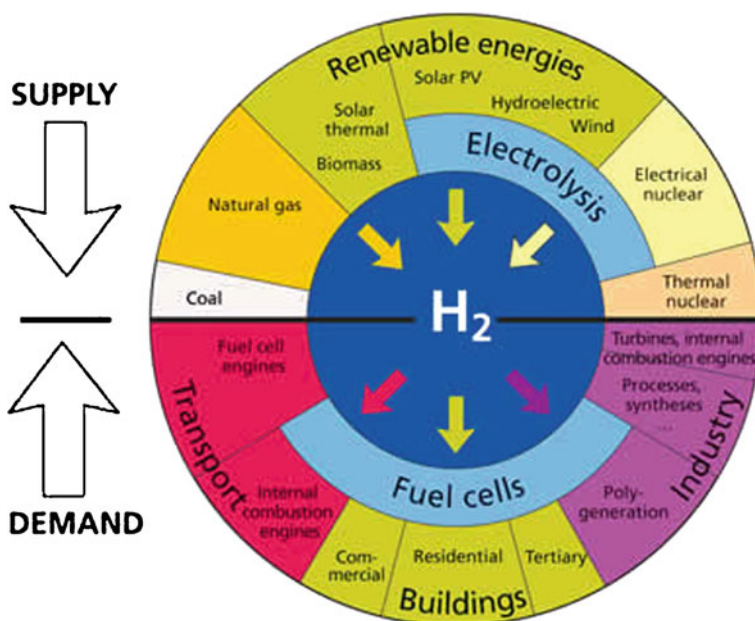


Fig. 2.6 Summary of the hydrogen economy. *Upper part* production, *lower part* uses [23]

few ppm of CO, the hydrogen going out from a conventional reformer needs to be purified by means of the following processes: two-steps water gas shift reactors followed by a separation/purification unit (PSA, Pd membrane, etc.), as reported in Fig. 2.7a [27].

Many researchers have proposed, as an economically more advantageous method, the use of a process able to produce a pure hydrogen stream in only one system [28–33]. In this contest, dense palladium MRs are able to carry out both the reaction and separate pure hydrogen in the same device (Fig. 2.7b).

In fact, although, niobium (Nb), vanadium (V) and tantalum (Ta) offer higher hydrogen permeability than palladium in a temperature range between 0 and 700°C, as shown in Fig. 2.8, nevertheless these metals give a stronger surface resistance to hydrogen transport than the palladium (Pd). For this reason, dense palladium membranes are preferentially used.

The hydrogen molecular transport in the palladium membranes occurs through a solution/diffusion mechanism, which follows six different activated steps [35]:

- dissociation of molecular hydrogen at the gas/metal interface;
- adsorption of the atomic hydrogen on membrane surface;
- dissolution of atomic hydrogen into the palladium matrix;
- diffusion of atomic hydrogen through the membrane;
- re-combination of atomic hydrogen to form hydrogen molecules at the gas/metal interface;
- desorption of hydrogen molecules.

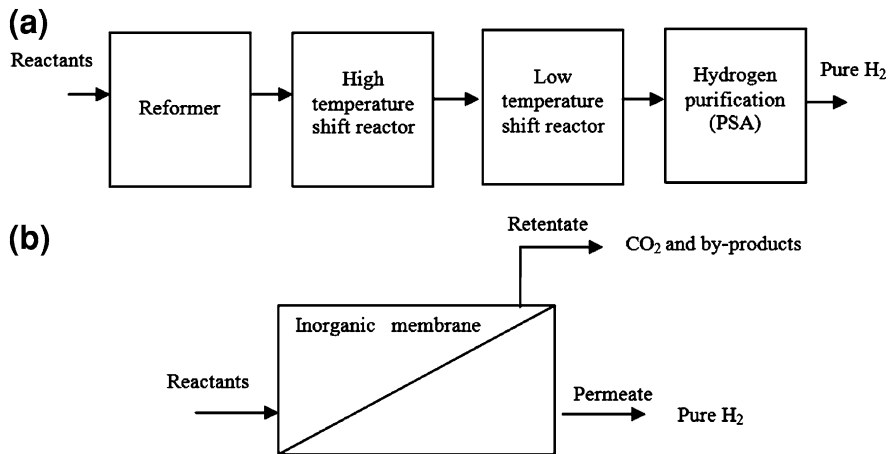


Fig. 2.7 Scheme of pure hydrogen production by hydrocarbons compounds steam reforming: traditional scheme (a) and inorganic membrane reactor (b) [28]

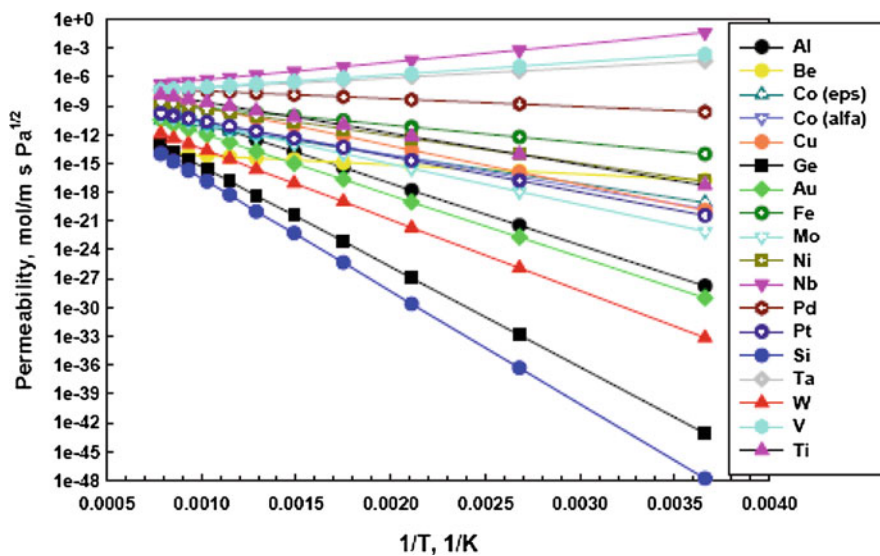


Fig. 2.8 Hydrogen permeability through different metals [34]

Depending on temperature, pressure, gas mixture composition and thickness of the membrane, each one of these steps may control hydrogen permeation through the dense film [28]. As a result, the hydrogen permeating flux can be expressed by means of the following equation:

$$J_{H_2} = Pe_{H_2} / \delta \cdot (p_{H_2,ret}^n - p_{H_2,perm}^n) \quad (2.2)$$

where n (variable in the range 0.5–1) is the dependence factor of the hydrogen flux to the hydrogen partial pressure, J_{H_2} the hydrogen flux permeating through the membrane, Pe the hydrogen permeability, δ the membrane thickness, $p_{H_2,ret}$ and $p_{H_2,perm}$ the hydrogen partial pressures in the retentate (the reaction side) and permeate sides (the volume in which the hydrogen permeating through the membrane is collected), respectively.

This equation even points out the inverse proportionality to the membrane thickness. The role of the membrane thickness is very important: on one hand, a thinner membrane offers a higher permeability; on the other hand, thicker membranes are necessary in order to ensure the mechanical resistance and strength.

When the pressure is relatively low, the diffusion is assumed to be the rate-limiting step and the factor n is equal to 0.5. In this case, Eq. 2.2 becomes the Sieverts–Fick law [36]:

$$J_{H_2, \text{Sieverts–Fick}} = Pe_{H_2} / \delta \cdot \left(p_{H_2,ret}^{0.5} - p_{H_2,perm}^{0.5} \right) \quad (2.3)$$

On the contrary, at high pressures the hydrogen–hydrogen interactions in the palladium bulk are not negligible. In this case, n becomes equal to 1:

$$J_{H_2} = Pe_{H_2} / \delta \cdot (p_{H_2,ret} - p_{H_2,perm}) \quad (2.4)$$

The relationship between hydrogen permeability and temperature follows an Arrhenius behaviour (Eq. 2.5), while “ n ” generally does not depend on the temperature:

$$Pe_{H_2} = Pe_{H_2}^0 \exp(-E_a/RT) \quad (2.5)$$

where Pe_0 is the pre-exponential factor, E_a the apparent activation energy, R the universal gas constant and T the absolute temperature.

As a consequence, when Sieverts–Fick law is valid, the hydrogen flux is written in terms of the so-called Richardson’s equation:

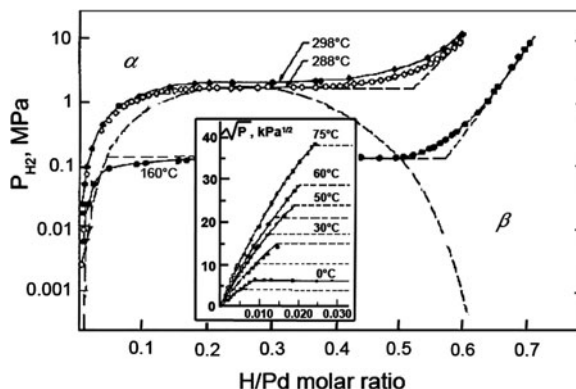
$$J_{H_2} = Pe_{H_2}^0 [\exp(-E_a/RT)] \left(p_{H_2,ret}^{0.5} - p_{H_2,perm}^{0.5} \right) / \delta \quad (2.6)$$

Nevertheless, although the pure palladium membranes are characterized by a complete hydrogen perm-selectivity, their commercialization is limited by some drawbacks such as relatively low hydrogen permeability and high cost [37].

2.3.1 Problems Associated with the Pure Palladium Membranes

The most important problem associated with the use of pure palladium membranes is the “hydrogen embrittlement” phenomenon. When the temperature is below 300°C and the pressure below 2.0 MPa, the β -hydride phase may nucleate from the

Fig. 2.9 Equilibrium solubility isotherms of PdH_n for bulk Pd at different temperatures [42]



α -phase, resulting in severe lattice strains (see Fig. 2.9), so that a pure palladium membrane becomes brittle after a few cycles of $\alpha \rightleftharpoons \beta$ transitions [38–40].

These transitions do not take place as a change of the lattice structure, but as a lattice dilatation. The β -hydride phase formation is represented as a clustering of hydrogen atoms, whose energy of attraction, being associated with the lattice, strains around the dissolved hydrogen atom [41].

A possible solution to avoid this phenomenon is represented by the use of a Pd-alloy containing another metal, such as silver. The role of silver is explained by its electron donating behaviour, being largely similar to the one of the hydrogen atom in palladium. Silver and hydrogen atoms would compete for the filling of electron holes [42].

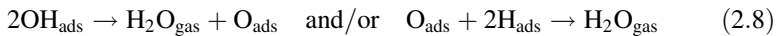
Another critical problem is represented by the palladium surface contamination of Hg vapour, hydrogen sulphide, SO_2 , thiophene, arsenic, unsaturated hydrocarbons, chlorine carbon from organic materials. In particular:

- *Poisoning of sulphur compounds*: Pd-coated membranes could rapidly be destroyed after exposure to a gas stream containing hydrogen sulphide and the poisoning effects are irreversible [43, 44]. Palladium becomes palladium sulphide, whose lattice constant is twice than of pure Pd and, thus, the structural stress leads to the formation of cracks.
- *Poisoning of CO*: the presence of CO in a feed gas stream could cause a decrease in the hydrogen permeation flux, because the adsorbed CO displaces the adsorbed hydrogen and further blocks hydrogen adsorption sites [45]. Moreover, this reduction becomes more significant at low temperature (below 150°C) or high CO concentration [46]. CO is adsorbed on the palladium surface blocking available dissociation sites for hydrogen. In order to improve the chemical stability of the metal membranes it is possible:
 - to use different types of Pd alloys constituted by other metals such as Cu, Ni, Fe, Pt and Ag,
 - to prepare nanostructured or amorphous thin alloy membranes.

- *Poisoning of H₂O*: the presence of water vapour has a more negative effect on hydrogen permeability than the presence of CO [47]. The adsorbed water molecules dissociate on the surface of the Pd film:



where the H_{ads} may permeate into the bulk of the Pd film [48]. H_2O is recombined through these reactions:



Therefore, the process of H_2O dissociation/recombinative desorption contaminates the palladium surface with adsorbed O.

- *Poisoning of coke*: both hydrogen permeance and perm-selectivity of a thin palladium membrane decrease after it is brought in contact with coke at elevated temperature [49]. This phenomenon can be addressed for the fact that carbon atoms penetrate into the palladium lattice and cause the failure of the membrane owing to the expansion of the palladium lattice.

Moreover, the palladium membranes are still very expensive. In order to reduce their cost it is possible to develop low palladium content based alloy trying to reduce the Pd-based layer thickness [50–52].

2.4 Palladium-based Membranes

Generally, the palladium-based membranes can be subdivided into supported and laminated ones. In the *supported membranes*, a thin dense layer of a palladium alloy is deposited onto a porous support such as porous Vycor glass (silica gel). Nevertheless, using this kind of support, the palladium layer is easily stripped off owing to the loss of an anchor effect [53].

Other types of porous glass materials are represented by SiO_2 , Al_2O_3 and B_2O_3 , giving excellent anchor effect and adherence [53]. Also porous stainless steel (PSS) can be considered as a valid support due to its mechanical durability, its thermal expansion coefficient close to that of palladium and the ease of gas sealing [53].

The upper temperature limits of the supported membranes depend on: the material, the chemical atmosphere and the support characteristics such as porosity and pore diameter [54].

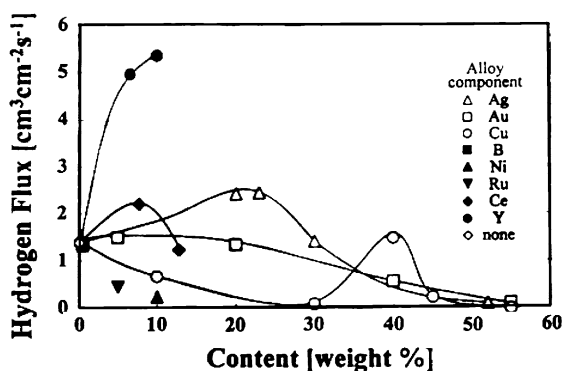
In the *laminated membranes*, thin palladium (or palladium alloys) layer avoids the formation of oxides on the metallic surfaces resulting in a reduction of the hydrogen adsorption activation energy and, as a consequence, in an increase of the hydrogen permeation flux [55].

Generally, the palladium alloys have some advantages with respect to the pure palladium membranes such as a reduced critical temperature for the α – β phase transition. For example, Pd–Ag membranes can operate in hydrogen atmosphere at

Table 2.2 Improvement in hydrogen permeability of various binary and tertiary palladium alloys at 350°C [57]

Alloy metal	wt% for maximum permeability	Normalized permeability ($Pe_{\text{alloy}}/Pe_{\text{Pd}}$)
Y	10.0	3.8
Ag	23.0	1.7
Ce	7.7	1.6
Cu	40.0	1.1
Au	5.0	1.1
Ru, In	0.5–6.0	2.8
Ag, Ru	30.2	2.2
Ag, Rh	19.1	2.6
Pure Pd	–	1.0

Fig. 2.10 Hydrogen flux through palladium alloy membranes against metal content [58]



temperatures below 300°C without observing embrittlement rather than pure palladium membranes [42]. Moreover, in some cases, the hydrogen permeability of palladium alloys is higher than pure palladium, as reported in Table 2.2. In fact, as shown in Fig. 2.10, the hydrogen flux through the Pd–Ag membranes reaches the maximum value at 350°C and 2.2 MPa with a 23% Ag content. In details, the permeability is 1.7 times higher than one of a pure Pd membrane. The Pd–Cu alloy even shows a maximum value of hydrogen flux with 40% Cu content, although these membranes suffer a permeation decrease when exposed at 900°C for a long time [56].

Moreover, the palladium alloys improve chemical resistance of the membranes. For example, Pd–Cu and Pd–Au increase the resistance to H₂S [59] as well as palladium-coated amorphous Zr–M–Ni (M = Ti, Hf) alloy membranes are resistant enough in a hydrogen atmosphere and have stable hydrogen permeability in the range of 200–300°C [60].

In order to further reduce the membrane cost, low palladium content based alloys can be produced [52]. In fact, Basile et al. [61] demonstrated that thin dense Ti–Ni–Pd membranes with a low palladium content (4.17 vs 77.0% of the Pd–Ag

and 60.0% of the Pd–Cu) make this membrane still competitive from an economical point of view.

2.4.1 Methods for Producing Palladium-based Membranes

Palladium-based membranes can be produced by several methods, depending on some factors such as the nature of the metal itself, the manufacturing facilities, required thickness, surface area, shape, purity, etc. Nevertheless, no one method can produce a membrane, which combines advantageously all these factors. Therefore, the choice of the production method becomes a compromise between these factors [42]. At lab-scale, the thickness as well as the continuity and imperviousness of the film are considered the most important factors [42]. In particular, in the last few years, the main aim has been to reduce the thickness of the palladium-based films.

Criscuoli et al. [62], for example, carried out an economical analysis of palladium-based MRs, comparing the costs between the conventional apparatus and different membrane systems for pure hydrogen production. In particular, the authors studied the effect of the palladium thickness and membrane permeability to hydrogen on the costs of membrane devices. They demonstrated that both higher permeabilities and lower thickness improve the hydrogen removal leading to a decrease in membrane area for a pure hydrogen recovery and a cost reduction. The authors concluded that MRs could represent a possible alternative to conventional apparatus for palladium thicknesses equal or lower than 20 μm . Moreover, the authors highlighted that current methods of preparing palladium-based membranes are still expensive due to the inadequate productivity per unit membrane area. A cost reduction for the Pd-based membranes could be achieved through a massive production as detailed in Chap. 3.

The most important production methods of palladium-based membranes are described in the following.

The *Conventional cold rolling* is the most diffuse technique for producing metallic plates or sheets at laboratory scale [63]. It involves:

- melting the raw materials with chosen composition at very high temperature,
- ingot casting,
- high temperature homogenization,
- hot and cold forging or pressing, followed by repeated sequences of alternate cold rolling and anneals, down to the required thickness.

If the cooling speed of melts is fast, amorphous materials (*metallic glasses*) can be realized obtaining good characteristics such as high mechanical toughness, considerable corrosion resistance, good electronic properties, high catalytic activities, reversible hydrogen storage, etc. [64, 65]. The cold rolling treatment can enhance the hydrogen solubility in palladium and its alloys owing to the accumulation of hydrogen excess in the stress field around dislocations, formed during

the process. This effect can be gradually eliminated during annealing of the deformed membranes by increasing the temperature [66].

In *Physical vapour deposition* (PVD) method, the solid material to be deposited is evaporated in a vacuum system through physical techniques, followed by condensation and deposition as a thin film on a cooler substrate. PVD is a very versatile method for manufacturing of pure metal films, alloys or compounds of thickness up to 50 μm [67]. At relatively high temperature, a thermal treatment is generally necessary to homogenize the composition of a multilayer deposit [68].

Sputtering and magnetron sputtering (MS) is an evaporation technique used for PVD under vacuum. A sputtering system consists of a vacuum chamber containing a target (a plate of the material to be deposited) and the substrate (i.e., the membrane), in which a sputtering gas (an inert gas such as argon) is introduced to provide the medium in which a glow discharge, or plasma, may be initiated and maintained. Afterwards, positive ions strike the target and remove target atoms and ions by momentum exchange. The condensation of these species over the support produces a thin film. Before sputtering the metal, the ion bombardment of the support is carried out for cleaning its surface and improving the film adherence.

Spray pyrolysis is a very simple technique in which a metal salt solution is sprayed into a heated gas stream and, then, pyrolyzed. It could be useful in the case of not requiring very high purity of hydrogen due to the relatively low H_2 /other gases perm-selectivity shown by using this technique.

Compared to the other deposition techniques, the spray pyrolysis method shows quite low separation factor, indicating that the technique needs some improvements, especially for producing dense films.

Solvated metal atom deposition method (or co-condensation technique) allows an easy introduction of the metal phase on the inner surface of a tubular membrane. Palladium vapour obtained by the resistive heating of a crucible loaded with Pd shots is co-condensed in a typical glass reactor. At the end of the reaction, the flask is allowed to warm up to -40°C and the resulting yellow-brown solution siphones under argon and handles at low temperature, using the Schlenk tube technique. The amount of palladium in the isolated solution is determined by X-ray fluorescence. Palladium particles are deposited on the inner surface of a tubular membrane by filling the membrane tube (fitted with Teflon stoppers at the ends) with the above solution and heating up to room temperature.

In *Chemical vapour deposition* (CVD) process, a chemical reaction involving a metal complex in the gas phase is performed at a controlled temperature and the produced metal deposits as a thin film by nucleation and growth on the substrate [69]. The deposition takes place on the hot substrate positioned in the CVD reactor. As in the case of PVD technique, the reaction temperature can be reached either by resistive heating of the substrate or by other heating sources [70].

Electrochemical vapour deposition (EVD) is, essentially, a variation of the CVD technique. In the EVD process, for example, a porous substrate separates a mixture of chlorine vapours (ZCl_3 , YCl_3 , etc.) and an oxygen source (water vapour or oxygen) [11]. Initially, the reactants from both sides of the support inter-diffuse into the pores and form solid oxides, as in the CVD process. When the pores are

closed, oxygen ions are conducted across the solid oxide and the oxide film grows on the chlorine side.

In the *Electroplating* (EP) method, a substrate, used as a cathode, is coated with a metal or an alloy in a plating bath [71]. Palladium can be easily deposited in thick and ductile deposits, providing a good control on the composition of the bath, its temperature and current density [72]. The thickness of deposited films can be mastered by controlling electroplating time and current density [73, 74] and film values from a few microns up to millimetres can be obtained. However, the large domains of alloy composition is not easy to control since the relative deposition of two metals simultaneously from the same solution depends on the simplicity of controlling chemical complexing in the bath [11].

The *Electroless plating deposition* (ELP) technique is based upon the controlled auto-catalyzed decomposition or reduction of meta-stable metallic salt complexes on target surfaces [75]. In the case of palladium, usually, the substrate should be pre-seeded with palladium nuclei in an activation solution in order to reduce the induction period of the autocatalytic plating reaction. For some applications, this technique provides strong benefits such as uniformity of deposits on complex shapes and hardness. Palladium and some of its alloys are among the few metals that can be deposited in this way [11]. However, this method presents some drawbacks such as difficult thickness control, costly losses of palladium in the bath, not guaranteed purity of the deposit and so on [75].

Sol-gel technique is a technique adopted for the preparation of thin materials on which the morphological characteristics (e.g., thickness and porosity) must be accurately controlled. Composite membranes resulting from this process are usually microporous and mesoporous, in which permeation of gases is mainly controlled by surface transport and/or the Knudsen flow mechanism [11].

Molecular layering (ML) technique is one of the most promising methods of membrane modification at the atomic level [76, 77]. The ML method is based on the chemisorption of reagents on a solid substrate surface and consists of the irreversible interaction of low-molecular reagents and functional groups of a solid substrate surface under the conditions of continuous reagent feed and the subsequent removal of the formed gaseous products.

However, each aforementioned method presents benefits and drawbacks. For example, both CVD and ELP techniques are able to coat a complex-shaped component with a uniform thickness layer. Unfortunately, non desired compounds and impurities can be formed and incorporated in the palladium layer, reducing the flux of hydrogen through the film. Moreover, by ELP method, it is not easy to control the thickness of the film. On the contrary, an important benefit of the electroless coating is that it is well suited to applications on available commercial tubular membranes. CVD is not an economic process due to the strict conditions required for the process.

In conclusion, Table 2.3 reports the permeation data of different palladium-based composite membranes, produced, principally, by ELP or CVD techniques. Many parameters are reported in the table: membrane type and thickness, temperature and pressure ranges of the permeation experiments, hydrogen flux,

Table 2.3 Permeation data of different palladium-based membranes reported in the literature

Membrane type	T (°C)	Δp (bar)	δ (μm)	J_{H_2} ($\text{mol}/\text{m}^2 \text{ s}$)	$P_{\text{eff}, \text{H}_2}$ ($\text{mol m}/\text{m}^2 \text{ s Pa}$)	$\phi_{\text{H}_2}/\text{N}_2$	Preparation method	References
Pd/PSS	520	1.5	10	1.8×10^{-1}	1.2×10^{-11}	–	ELP	[61]
Ti–Ni–Pd	450	3.0	45	$\sim 3.3 \times 10^{-3}$	1.7×10^{-10}	∞	Cold rolling	[61]
Pd/PSS-YSZ	400	–	7–10	2.5×10^{-2}	4.7×10^{-9}	800–900	ELP	[78]
Pd/ Al_2O_3	200	0.1	15	2.2×10^{-1}	3.3×10^{-10}	7	ELP	[79]
Pd/glass	350–500	4.0	2	–	3.4×10^{-12}	1140–12900	ELP	[80]
Pd/ Al_2O_3	450	–	4.8	–	1.4×10^{-11}	60	ELP	[81]
Pd/ Al_2O_3	300	0.3	2–4	$1.0\text{--}2.0 \times 10^{-1}$	$1.3\text{--}2.7 \times 10^{-11}$	5000	CVD	[82]
Pd/ Al_2O_3	528	–	2–3	–	3.5×10^{-12}	<18	ELP	[83]
Pd/ Al_2O_3	400	1.0	5	1.6×10^{-1}	7.8×10^{-12}	100–200	ELP	[84]
Pd/ BaZrO_3	600	–	41	–	–	5.7	CVD	[85]
Pd/MPSS	500	1.0	6	3.0×10^{-1}	1.8×10^{-11}	–	ELP	[86]
Pd/PNS	500	3.6	–	8.3×10^{-2}	–	3.7	MS	[87]
Pd/ ZrO_2 /PSS	500	1.0	10	8.3×10^{-2}	8.3×10^{-11}	–	ELP	[88]
Pd/ $\alpha\text{Al}_2\text{O}_3$	370	2.9	1	4.0×10^{-1}	–	3000–8000	ELP	[89]
Pd ₈₄ –Cu ₁₆ / ZrO_2 –PSS	480	2.5	5	6.0×10^{-1}	2.6×10^{-9}	∞	ELP	[90]
Pd ₉₀ –Ag ₁₀ / $\alpha\text{Al}_2\text{O}_3$	200–343	0.8–2.5	20	1.4×10^{-1}	2.5×10^{-11}	30–178	ELP	[91]
Pd–Ag/ Al_2O_3	–	1.4	10	1.0×10^{-1}	1.0×10^{-11}	1500	ELP	[92]
Pd–Ag/PSS	400–500	1.0	2–3	3.0×10^{-1}	6.0×10^{-12}	–	ELP	[93]
Pd/ $\alpha\text{Al}_2\text{O}_3$	550	4.0	11	7.0×10^{-2}	–	~ 1000	ELP	[94]
Pd–Cu/ $\alpha\text{Al}_2\text{O}_3$	450	3.5	11	8.0×10^{-1}	2.6×10^{-11}	1150	ELP	[95]

hydrogen permeance, ideal separation factor, preparation method of the metallic thin layer and relative bibliography. Generally, it is possible to state that the porous palladium-based membranes show high hydrogen flux and low hydrogen selectivity, while dense palladium-based membranes show low hydrogen flux and high hydrogen selectivity.

2.5 Reaction Processes Using Palladium-based Membranes

The first use of palladium membranes was registered in the 1866, when Graham used a palladium membrane to separate hydrogen from gases mixtures [96]. In 1915, Snelling patented the hydrogen removal through palladium or platinum tubes from a reactor using a granular catalyst for dehydrogenation reactions [53]. In 1964, Gryaznov proposed as a novel application of palladium-based membranes a method for carrying out simultaneously the evolution and the consumption of hydrogen in a dense tubular palladium reactor, where palladium is permeable only to hydrogen and also serves as a catalyst.

The first commercial application of a dense 23 wt% Pd–Ag membrane was in the 1964, when Johnson Matthey used this membrane for purifying a hydrogen rich-stream [97]. Successively, Johnson Matthey also developed a hydrogen generator constituted by a palladium MR fed with a methanol/water mixture. This plant was used in small scale by British Antarctic Survey in 1975 [98, 99].

Moreover, the first pilot-scale composite palladium MR for direct ultra-pure hydrogen production has been realized by the largest gas company in Tokyo (Tokyo Gas Company Ltd.) [100].

Recently, a reformer and membrane modules (RMM) test plant having the capacity of 20 Nm³/h of hydrogen has been designed and constructed by Tecnimont KT near Chieti, in Italy. This plant is described in Chap. 10 of this book.

Actually, the palladium-based MR represents an alternative solution to conventional systems for pure hydrogen production to be supplied to a PEMFC.

In fact, the palladium-based MR, combining in only one unit the separation phase with the reaction steps, offers the following advantages with respect to a FBR:

- to combine the chemical reaction and the gas separation in only one system reducing the capital costs,
- to enhance the conversion of equilibrium limited reactions. In fact, by the selective removal of one or more products from the reaction side, the thermodynamic equilibrium restrictions can be overcome, due to the so-called “shift effect”,
- to achieve higher conversions than FBRs, operating at the same MR conditions, or, on the contrary, the same conversion but operating at milder conditions,
- to improve products yield and selectivity,
- and, especially, to produce a pure hydrogen stream.

Table 2.4 Chemical reactions for producing pure hydrogen by using a palladium-based MR

Kind of reaction	Membrane	Material
Coupling of hydrogenation and dehydrogenation reactions	Dense	Pd
Decomposition of RuO_4 to $\text{RuO}_2 + \text{O}_2$	Dense	Pd/Ag
Decomposition of ammonia	Dense	Pd
Dehydrogenation of cyclohexane to benzene	Dense	Pd/Ag
Dehydrogenation of ethylbenzene to styrene	Porous	Pd
Dehydrogenation of ethane to ethylene	Dense	Pd/Ag
Dehydrogenation of isopropyl alcohol to acetone	Dense	Pd
Dehydrogenation of water–gas shift reaction	Dense	Pd, Pd/Ag
	Porous	Pd
Dehydrogenation of <i>n</i> -heptane to toluene + benzene	Dense	Pd/Rh
Dehydrogenation of butane to butadiene	Dense	Pd
Dehydrogenation of 1,2-cyclohexanediol	Dense	Pd/Cu
Dry reforming of methane	Dense	Pd-alloy
Hydrogenation of ethylene to ethane	Dense	Pd
Hydrogenation of butadiene	Dense	Pd
Hydrogenation of acetylene	Dense	Pd/Ag
Hydrogenation of butenes	Dense	Pd/Sb
Hydrogenation of diene hydrocarbons	Dense	Pd/Ru
Hydrogenation of phenol to cyclohexanone	Dense	Pd; $\text{Pd}_{93}\text{Ni}_7$; $\text{Pd}_{93}\text{Ru}_7$; $\text{Pd}_{77}\text{Ag}_{23}$
Hydrodealkylation of dimethylnaphthalenes	Dense	Pd/Ni
Methane conversion into hydrogen and higher hydrocarbons	Porous	Pd-alloy
Octane reforming	Dense	Pd and Pd-alloy
Partial oxidation of methane	Porous	Pd-alloy
Steam reforming of ethanol	Dense	Pd and Pd-alloy
Steam reforming of methane	Dense	Pd-alloy
Steam reforming of methanol	Dense	Pd and Pd-alloy

In order to produce pure hydrogen stream by using a palladium-based MR, many chemical reactions can be used. Some of them are reported in Table 2.4.

In this chapter, a particular attention will be address to the following reactions:

- methane steam reforming,
- dry reforming of methane,
- water gas shift,
- ethanol steam reforming,
- methanol steam reforming,
- bioglycerol steam reforming,
- acetic acid steam reforming.

Moreover, in order to solve the problems related to the environmental pollution, previously mentioned, it will be interesting to investigate the hydrogen production via reforming reactions of bio-fuels such as methanol, glycerol, ethanol, biogas,

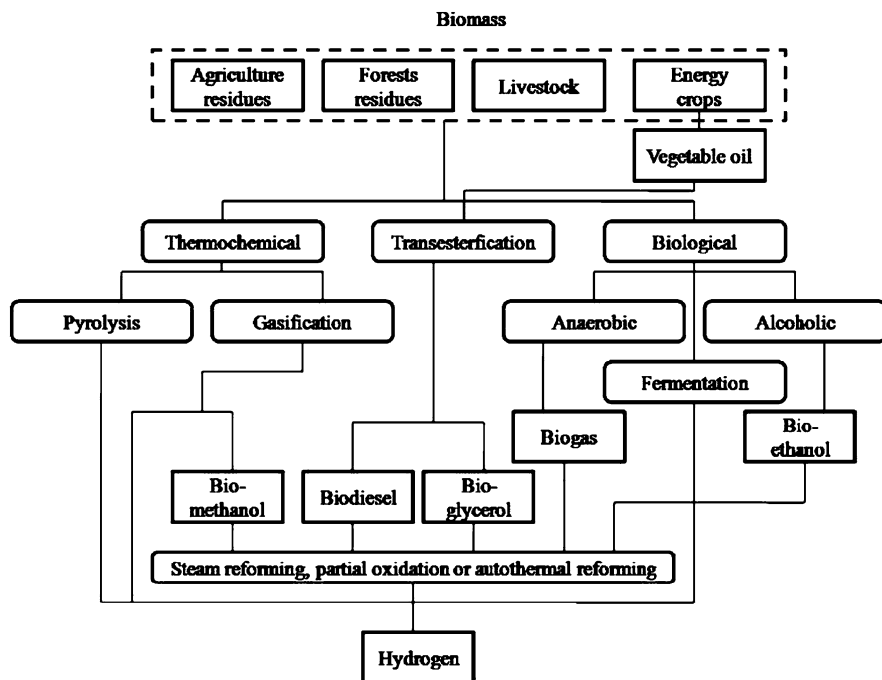
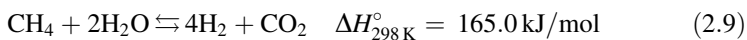


Fig. 2.11 Selected hydrogen production technologies from various renewable sources [101]

etc., which can be produced by renewable sources such as biomass, as reported in Fig. 2.11.

2.5.1 Methane Steam Reforming

Generally, methane steam reforming (MSR) reaction is carried out in FBRs between 800 and 900°C due to the endothermicity of the reaction [27].



Only at this elevated temperature, the methane conversion is complete. Furthermore, in the strenuous conditions, the catalyst undergoes deactivation due to carbon formation. As an alternative, using Pd-based MRs it is possible to reach complete methane conversion at lower temperature ($\sim 500^\circ\text{C}$) as summarized in Table 2.5. For example, Lin et al. [102, 103], carried out the MSR reaction in a palladium-based MR, obtaining methane conversions exceeding 80% at temperature between 350 and 500°C rather than 850°C, necessary in a FBR. Chen et al. [104] obtained almost 100% methane conversion at 550°C with respect to 27% obtained in a FBR. In particular, the authors reached 95% pure hydrogen recovery,

Table 2.5 Methane conversion and pure hydrogen recovery data for methane steam reforming reaction

Membrane	T (°C)	p_{reaction} (bar)	MR conversion (%)	FBR conversion (%)	Pure hydrogen recovery (%)	References
Pd-SS	500	20.0	85	–	90	[103]
		9.0	40	20	30	
Pd/Al ₂ O ₃	550	9.0	99	27	95	[104]
Pd/Vycor	500	1.0–9.1	90	–	–	[105]
Pd/5.1%Ag	500	1.4	50	35	–	[106]
Pd-23% Ag	500	6.1	50	~ 20	–	[107]
				(equilibrium)		
		10.0	60		–	
Pd-based	500	1.0	100	–	–	[108]
Pd-25%Ag	150	1.0	15.4	12.7	–	[109]
	300		16.5	16.5	–	
Pd-PSS	527	3.0	100	~ 50	–	[110]
Pd-based	650	2.0–4.0	97	–	–	[111]

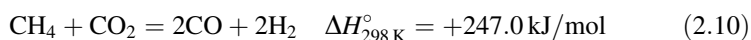
confirming that the selective removal of hydrogen from the reaction zone allows to obtain methane conversion significantly higher than a FBR.

Generally, Table 2.5 shows that the palladium-based MRs application allows reducing the operative conditions required for carrying out the MSR reaction in a FBR and to obtain high methane conversion as well as high pure hydrogen recovery.

Chapter 5 will report a detailed assessment of methane steam reforming MR performance. Moreover, it has to be cited the test plant fabricated by Tecnimont KT and described in Chap. 10, which is composed by a series of reformer reactors and Pd-based membrane separators and has a capacity of 20 Nm³/h of pure H₂ production.

2.5.2 Dry Reforming of Methane

One of the most important drawback related to the methane dry reforming reaction is the carbon deposition.



This was highlighted by different scientists such as Galuszka et al. [112], who observed coke deposition carrying out the reaction (2.10) at 550–600°C in both FBR and MR (housing a dense palladium membrane prepared by electroless plating technique). Gallucci et al. [113] performed the methane dry reforming reaction in FBR and both porous and dense Pd–Ag MRs at 400 and 450°C. The authors demonstrated that the MRs give lower carbon deposition with respect to

Table 2.6 Methane conversion data for methane dry reforming reaction

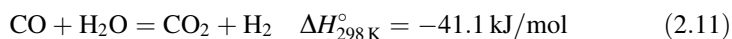
Membrane	T (°C)	MR conversion (%)	FBR conversion (%)	References
Pd-based	550	37.5	17.2	[112]
	600	48.6	40.9	
Porous Pd–Ag	400	2.1	5.6	[113]
	450	8.4	17.4	
Dense Pd–Ag	400	7.9	5.6	[114]
	450	17.8	17.4	
Pd/ceramic composite	500	54	–	[115]

the FBR and, in particular, the lower carbon deposition is obtained when the dense membrane is used.

In this case, the palladium-based MR benefits result in higher methane conversion than FBR, as shown in Table 2.6, and a reduction of the carbon deposition with respect to a conventional reformer, as above reported.

2.5.3 Water Gas Shift Reaction

The water gas shift (WGS) reaction is one of the most important industrial processes used to produce hydrogen:



The applications and the research studies performed on this kind of reaction were realized by many scientists. In particular, a great literature is present on this issue concerning the use of palladium-based membrane reactors, as resumed briefly in Table 2.7, where CO conversion values obtained in MR and compared with the thermodynamic equilibrium ones of some scientific works are reported. In particular, among these works, Kikuchi et al. [115] demonstrated that, using a 20 μm layer of palladium-coated onto a porous glass tube produced by the electroless plating method, allows to obtain almost complete CO conversion.

Basile et al. [116] studied the WGS reaction using a MR consisting of a composite palladium-based membrane realized with an ultrathin palladium film ($\sim 0.1 \mu\text{m}$) coated on the inner surface of a porous ceramic support ($\gamma\text{-Al}_2\text{O}_3$) by the co-condensation technique. The authors pointed out the benefit of applying a palladium MR, taking into account that, at 320°C and 1.1 bar, the thermodynamic equilibrium of CO conversion is around 70%, while the authors obtained with the MR CO conversion of around 100%. Moreover, the same authors illustrated that a complete CO conversion could be reached by using a composite membrane with a thinner palladium layer (10 μm Pd film coated on a ceramic support) [117].

Moreover, Iyoha et al. [118] observed that the CO conversion can decrease from around 90% to around 70% once a palladium MR is replaced with another

Table 2.7 CO conversion data for water gas shift reaction

Membrane	T (°C)	p_{reaction} (bar)	MR conversion (%)	FBR conversion (%)	References
Pd/Vycor	400	1.0	92	76	[115]
Pd/ γ -Al ₂ O ₃	320	1.1	100	84	[116]
Pd on ceramic	320	1.0	98	83	[117]
Pure Pd	900	2.4	93	—	[118]
Pd ₈₀ -Cu ₂₀			66		
Pd on porous glass	400	1.0	98	75	[119]
Pd-composite	322	1.1	99.2	99.1	[120]
		1.2	99.9		
Pd-Ag	325	1.0	100	84	[121]
Pure Pd	320	1.3–1.5	100	<50	[122]
Mesoporous Pd			78		
Pd(60%)-Cu	350	—	94	93	[123]

MR containing a Pd₈₀Cu₂₀ membrane, due to the lower hydrogen permeance of the Pd/Cu membrane.

In Table 2.7, the comparison between the CO conversion values obtained in different palladium-based MRs and the equilibrium ones is reported, demonstrating the capacity of palladium-based MRs to overcome the thermodynamic limits and to obtain high CO conversion. Chapter 7 reports a detailed assessment of selective membrane application for WGS process.

2.5.4 Ethanol Steam Reforming

Bioethanol is an aqueous solution containing between 8.0 and 12.0 wt% of ethanol and some by-products depending on the raw material used [124]. Nevertheless, the bioethanol distillation is an expensive process, because of the azeotrope presence. For this reason, in the last years, bioethanol is directly used as fuel in steam reforming reaction. Moreover, an excess of water improves the palladium-based MR performances reducing also the CO content as by-products.



A great part of scientific literature is focused on carrying out this reaction using ethanol produced by no-renewable sources [125–130]. Concerning bioethanol steam reforming (BESR) reaction, only few studies are deal with both FBRs [131–133] and MRs use [134–136], as reported in Table 2.8.

In particular, Gernot et al. [134] used a composite Pd-based MR, whose structure consists of a three layers stacking. This membrane structure lowers the thermal expansion stresses between the membrane and the support as well as the quantity of noble metal active layer. At 600°C and for 500 h of work, as best

Table 2.8 Ethanol conversion and pure hydrogen recovery data for bioethanol steam reforming reaction

Membrane	T (°C)	p_{reaction} (bar)	MR conversion (%)	FBR conversion (%)	Pure hydrogen recovery (%)	References
Pd-based	600	–	100	–	–	[134]
Dense	400	1.5	95	60	30	[135]
Pd–Ag						
Dense	400	3.0	100	65	95	[136]
Pd–Ag						

results the authors achieved a complete bioethanol conversion as well as a pure hydrogen stream collected with an impurity content <1.0%.

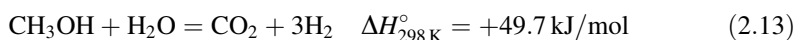
Julianelli et al. [135, 136] studied from an experimental point of view the steam reforming reaction of a simulated bioethanol mixture (water/ethanol feed molar ratio = 18.7/1 mol/mol without other typical by-products) in a dense Pd–Ag MR in order to produce pure hydrogen. The dense Pd–Ag membrane was prepared by cold rolling and diffusion welding technique [137]. As reported in the table, working at 400°C and 3.0 bar, the authors obtained a complete bioethanol conversion (~85.0% for the FBR working at the same MR operating conditions) and around 95.0% of pure hydrogen recovery.

However, Table 2.8 shows the capacity of palladium-based MRs to obtain higher ethanol conversions than the FBRs.

2.5.5 Methanol Steam Reforming

Methanol is conventionally produced from natural gas [138]. Alternatively, methanol can be obtained from biomass, such as wood and agricultural waste [102]. Renewable methanol presents different advantages as fuel and raw material. For example, it is more easily transportable than methane or other fuel gases, it has high energy density and does not require desulphurization.

Methanol steam reforming (SRM) (3.15) is an endothermic reaction, feasible at temperatures of 200–300°C [31].



As indicated in Table 2.9, Wieland et al. [31] carried out the SRM reaction using three different palladium-based MRs (Pd₇₅–Ag₂₅, Pd₆₀–Cu₄₀ and Pd–V–Pd). Owing to the low stability of the vanadium-based membrane at pressures above 4.2 bar, the authors compared the performances of the SRM reaction when carried out in a Pd–Ag and a Pd–Cu MRs. The authors showed that a higher pure hydrogen recovery is obtained using the Pd–Ag MR (at 25.0 bar, 300°C, the hydrogen recovery of Pd–Ag MR is 96.0% against 78.0% of the Pd–Cu MR).

Table 2.9 Methanol conversion and pure hydrogen recovery data for methanol steam reforming reaction

Membrane	T (°C)	p_{reaction} (bar)	MR conversion (%)	FBR conversion (%)	Pure hydrogen recovery (%)	References
Pd–Ag	300	25.0	–	–	96	[31]
Pd–Cu					78	
Composite Pd–Ag	450	5.2	76		15	[33]
	550	5.2	73	–	45	
		7.9	72		50	
		11.4	71		53	
	600	11.4	75		60	
Dense Pd–Ag	250	1.3	80	40	–	[140]
TiO ₂ –Al ₂ O ₃ asymmetric porous commercial membrane with a Pd–Ag deposit	350		30		–	
	600		100		–	
Asymmetric porous ceramic membrane with a Pd–Ag deposit	350	1.3	45	86	–	[142]
	550		65		–	
Pine-hole free Pd–Ag thin wall membrane tube	350		87		–	
	450		100		–	
Dense Pd–Ag	300	1.3	100	55	–	[143]
Dense Pd–Ag	300	3.0	–	–	93	[144, 145]

Lin et al. [102, 139] used a double-jacketed supported palladium MR packed with Cu/ZnO/Al₂O₃ catalyst. The authors obtained a pure hydrogen recovery over 70.0%, concluding that this process can constitute an alternative solution of on-board hydrogen generation for electric vehicle fuel cells.

Basile et al. [140] compared the performances in terms of methanol conversion and pure hydrogen production with respect to the ones of a FBR. The authors demonstrated that the MR gives a higher methanol conversion at each operating condition investigated. As best results, a 80.0% methanol conversion is reached working at 250°C and 1.3 bar, as reported in Table 2.9.

Arstad et al. [141] used a self-supported, Pd/(23 wt%) Ag-based MR (with a thickness of 1.6 μm) achieving 100.0% the production of pure hydrogen. Hence, the authors concluded that the low-thickness of the palladium-based membrane can represent a fundamental step for reducing the palladium-cost and making competitive the hydrogen separation technologies by palladium-based membrane.

2.5.6 Bioglycerol Steam Reforming

Bioglycerol is a byproduct of biodiesel production [146], which is usually derived from the transesterification of vegetable oil with methanol or ethanol. During the

Table 2.10 Glycerol conversion and pure hydrogen recovery data for glycerol steam reforming reaction

Membrane	T (°C)	p_{reaction} (bar)	MR conversion (%)	FBR conversion (%)	Pure hydrogen recovery (%)	References
Dense Pd–Ag	400	4.0	94	40	60	[148]
Dense Pd–Ag	400	5.0	60	42	58	[149]

process, the oil is mixed with a metallic base (sodium or potassium hydroxide) and an alcohol (methanol or ethanol). The reaction produces methyl or ethyl ester (biodiesel) and glycerol as a byproduct, which can be used as a renewable source [147]. To the best of our knowledge, at moment, only Iulianelli et al. [148, 149] studied glycerol steam reforming (GSR) reaction in a dense Pd–Ag MR, as reported in Table 2.10.



The authors studied the catalyst influence on the reactor performances (glycerol conversion and pure hydrogen recovery), using two commercial catalysts: Co/Al₂O₃ and Ru/Al₂O₃. Using the Co/Al₂O₃ catalyst and at 4.0 bar and 400°C, the authors obtained a glycerol conversion of 94.0% and a pure hydrogen recovery higher than 60.0%. On the contrary, using the Ru/Al₂O₃ catalyst, the authors achieved around 20.0% glycerol conversion and 16.0% pure hydrogen recovery at 5.0 bar. Iulianelli justified these low performances as the main drawback due to the combination of ruthenium with an acid support as Al₂O₃, unfavourable for GSR reaction. Moreover, the authors observed that carbon formation, taking place during the reaction, affects negatively the performances of the Pd–Ag membrane in terms of a lower hydrogen permeated flux and catalyst deactivation.

2.5.7 Acetic Acid Steam Reforming

Acetic acid is a renewable source and can be easily obtained by fermentation of biomass [150]. Few studies [151–154] concerned the acetic acid steam reforming (AASR) reaction for producing hydrogen by means only FBRs.



Only two scientific papers were published dealing with the use of MR for carrying out the AASR reaction [155, 156], as shown in Table 2.11. In these studies, the AASR reaction was performed in a dense Pd–Ag MR packed with two kinds of catalyst: a Ni-based commercial catalyst in the first case and both

Table 2.11 Acid acetic conversion and pure hydrogen recovery data for acetic acid steam reforming reaction

Membrane	T (°C)	p_{reaction} (bar)	MR conversion (%)	FBR conversion (%)	Pure hydrogen recovery (%)	References
Dense	400	2.5	100	85	32	[155]
Pd–Ag (MR1)	450		100	75	36	
Dense	400	4.0	100	92	26	
Pd–Ag (MR2)	450		100	87	32	
Dense Pd–Ag	400		100	–	70	[156]

Ru-based and a Ni-based commercial catalyst in the second case. In both experiments, a complete acetic acid conversion was obtained.

2.6 Conclusions

An extensive overview concerning palladium-based membranes was presented, subsequently to a general classification of the membranes. In particular, an assessment of the problems associated with the pure palladium membranes was presented, which was followed by a description of the preparation methods of palladium-based membranes and their industrial applications.

In particular, this chapter highlighted the importance of palladium-based membranes for producing pure hydrogen. Applicability of these membranes is limited by sensitivity towards certain species and cost. When these membranes are applied to the reactor system, the MRs constitute an interesting alternative approach to the FBRs, owing to the ability of the palladium-based MRs in performing simultaneously the reaction process and the selective hydrogen separation. In this route, the continuous hydrogen removal permits to obtain higher reaction conversions than the thermodynamic equilibrium, which is the upper limit to be considered in a FBR. In the meanwhile, a pure hydrogen stream for directly feeding a PEMFC without needing any other purification process can be obtained.

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Membrane Reactors for Hydrogen Production
Processes

De Falco, M.; Marrelli, L.; Iaquaniello, G. (Eds.)

2011, XII, 235 p., Hardcover

ISBN: 978-0-85729-150-9