

Inorganic membranes for hydrogen production and purification: A critical review and perspective

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Received 1 April 2007; accepted 21 May 2007

Available online 29 May 2007

Abstract

Hydrogen as a high-quality and clean energy carrier has attracted renewed and ever-increasing attention around the world in recent years, mainly due to developments in fuel cells and environmental pressures including climate change issues. In thermochemical processes for hydrogen production from fossil fuels, separation and purification is a critical technology. Where water–gas shift reaction is involved for converting the carbon monoxide to hydrogen, membrane reactors show great promises for shifting the equilibrium. Membranes are also important to the subsequent purification of hydrogen. For hydrogen production and purification, there are generally two classes of membranes both being inorganic: dense phase metal and metal alloys, and porous ceramic membranes. Porous ceramic membranes are normally prepared by sol–gel or hydrothermal methods, and have high stability and durability in high temperature, harsh impurity and hydrothermal environments. In particular, microporous membranes show promises in water gas shift reaction at higher temperatures. In this article, we review the recent advances in both dense phase metal and porous ceramic membranes, and compare their separation properties and performance in membrane reactor systems. The preparation, characterization and permeation of the various membranes will be presented and discussed. We also aim to examine the critical issues in these membranes with respect to the technical and economical advantages and disadvantages. Discussions will also be made on the relevance and importance of membrane technology to the new generation of zero-emission power technologies.

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Keywords: Membranes; Dense metal membranes; Porous membranes; Hydrogen production; Hydrogen purification

1. Introduction

The concept of a hydrogen economy, a situation where hydrogen is used as the major carrier of energy, has been popular for many decades among futurists and some policy makers. The potential of hydrogen has been known for almost two centuries. The first combustion engine, developed in 1805 by Isaac de Rivaz, was fuelled with hydrogen. However, it was steam, and later petroleum, that have powered the world's engines so far.

Many countries around the world are seriously considering the implications of a shift towards a hydrogen economy. The growing interest in hydrogen is driven mainly by its potential to solve two major challenges confronting many of the world's economies, how to achieve energy independence while minimizing the environmental impact of economic activity. There are four critical technologies that need to be developed before a hydrogen economy could be realized:

- (1) Cost effective production of hydrogen in a carbon constrained global energy system. The challenges in this area include the production of H₂ from fossil fuels with carbon sequestration taken into account, and increasing utilization of renewable sources.

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- (2) Hydrogen purification and storage technologies that will be able to separate, and purify the hydrogen streams to the requirements of the subsequent storage and utilization systems. Efficient and practical storage devices for hydrogen will have to reach the US DOE target of 6.5 wt%.
- (3) An efficient, widely available and well managed hydrogen delivery and distribution infrastructure.
- (4) Efficient fuel cells and other energy conversion technologies that utilize hydrogen.

One of the promising candidates for hydrogen separation and purification is inorganic membrane, which has also shown increasing importance in membrane reactors in hydrogen production processes. So far there is no systematical review of the status of membranes for hydrogen applications. It is the aims of this review to provide an extensive assessment of the recent advances in both dense phase metal and porous ceramic membranes, and compare their separation properties and performance in membrane reactor systems in particular for natural gas reforming and the water gas shift reactions. The preparation, characterization and permeation of the various membranes will be presented and discussed. We also aim to highlight some critical issues in these membranes with respect to the technical and economical advantages and disadvantages.

1.1. Hydrogen as a fuel

Hydrogen is the most abundant element on the planet. It can be extracted from water, biomass, or hydrocarbons such as coal or natural gas. Hydrogen can also be produced by nuclear energy or via electricity derived from renewable resources such as wind, solar or biomass. Hydrogen is often referred to as ‘clean energy’ as its combustion produces only water, however, the production of hydrogen from hydrocarbons, yields CO₂, a greenhouse gas.

Globally, hydrogen is already produced in significant quantities (around 5 billion cubic metres per annum) and is used mainly to produce ammonia for fertiliser (about 50%), for oil refining (37%), methanol production (8%) and in the chemical and metallurgical industries (4%). With greater emphasis placed on environmental sustainability, energy cost and security (both for stationary and transport sectors), considerable efforts are now being directed at the developing the technologies required to build an infrastructure to support a “hydrogen economy.” Global investment in hydrogen has accelerated dramatically over the past few years and is now in the range of several US billion dollars. For instance, the Bush Administration recently announced a \$US1.7 billion program directed at advancing hydrogen technologies, in particular, fuel cell vehicles. Japan also recently announced plans to introduce around 4000 hydrogen filling stations by 2020.

Perhaps the best known example of a ‘hydrogen economy’ is Iceland which has set a goal for a complete transition to hydrogen by 2030. In this scenario, hydrogen will be produced via Iceland’s geothermal and hydro resources and fed into fuel cells for stationary applications (homes, businesses) and for transportation (cars, buses, fishing boats, etc.). Similarly, Hawaii is

currently conducting a feasibility study to assess the potential for large-scale use of hydrogen, fuel cells, and renewable energy.

A number of technological barriers need to be overcome in relation to hydrogen storage and distribution. The pathway to hydrogen is also still unclear. Many countries around the world have abundant resources in coal and gas, and these fossil fuels would play a key role in such a transition. Any major hydrogen initiative will also require significant investment in new infrastructure (pipelines, storage facilities, fuelling stations, etc.). Hydrogen promises to encourage diversity in a nation’s energy mix while potentially offering a cleaner environment.

1.2. H₂ production and purification needs

In thermochemical processes for hydrogen production from fossil fuels, separation and purification is a critical technology. Where water–gas shift reaction is involved for converting the carbon monoxide to hydrogen, membrane reactors show great promise for shifting the equilibrium. Membranes are also important to the subsequent purification of hydrogen. Hydrogen can be economically produced by steam reforming, a reaction between steam and hydrocarbons, using supported nickel catalysts. As CH₄ is a stable hydrocarbon, high temperatures (e.g., 800 °C) are required for the endothermic reaction:



Carbon monoxide is further reacted with steam to form H₂ and CO₂ by the exothermic reaction, which is commonly referred to as the water–gas shift reaction:



In order to obtain high purity hydrogen from either syngas or the products of the water–gas shift reaction (2), separation of H₂ from either CO or CO₂ is necessary. Competitive separation processes for hydrogen from such as streams include amine absorption (CO₂ separation), pressure swing adsorption (PSA) and membrane separation. Amine absorption processes are a very mature technology and will not be discussed further. From the experience of hydrogen separation in refineries, membrane systems are more economical than PSA in terms of both relative capital investment and unit recovery costs [1].

If H₂ is selectively removed from the reaction system, thermodynamic equilibria of these reactions are shifted to the products side, and higher conversions of CH₄ to H₂ and CO₂ can be attained and at even lower temperatures. Actually, enhanced performance of steam reforming with a real membrane catalytic system was firstly reported by Oertel et al. [2], consistent with computer simulation studies. They employed a Pd disk membrane with a thickness of 100 μm, which effectively enhanced hydrogen production, but at high temperatures of 700 or 800 °C. According to the calculation by Shu et al. [3], membrane separation can result in the significant conversion improvement on the CH₄ steam-reforming in a lower temperature range of 500–600 °C. At such moderate temperatures, commercially available Pd membranes are too thick to work effectively. The critical features of membrane for successful membrane reactors are

not only high separation selectivity, but also high permeability, which mean the rate of permeation should be comparable to the rate of catalytic reaction. Another important feature is the stability and durability of the membrane.

For hydrogen production and purification, there are generally two classes of membranes both being inorganic: dense phase metal, metal alloys and ceramics (perovskites), and porous ceramic membranes. Porous ceramic membranes are normally prepared by sol–gel or hydrothermal methods, and have high stability and durability in high temperature, harsh impurity and hydrothermal environments. In general, inorganic ceramic membranes possess lower H₂ selectivity but higher flux. In particular, microporous membranes show promise in water gas shift reaction at higher temperatures.

1.3. H₂ permselective membranes

1.3.1. Membranes and membrane separation

A membrane is a physical barrier allowing selective transport of mass species, widely used for separation and purification in many industries. Membranes can be classified into organic, inorganic and hybrids of organic/inorganic systems. Organic membranes can be further divided into polymeric and biological constituents, whilst inorganic ones to metallic (dense phase) and ceramic (porous and non-porous) membranes. Fig. 1 shows a schematic of the membrane separation process, in which the driving force is often pressure or concentration gradient across the membrane. An authoritative summary of basic concepts and definitions for membranes is available in an IUPAC (International Union of Pure and Applied Chemistry) report [4].

Criteria for selecting membranes are complex depending on the application. Important considerations on productivity and separation selectivity, as well as the membrane's durability and mechanical integrity at the operating conditions must be balanced against cost issues in all cases [5]. The relative importance of each of these requirements varies with the application. However, selectivity and permeation rate (or permeance) are

clearly the most basic properties of a membrane. The higher the selectivity, the more efficient the process, the lower the driving force (pressure ratio) required to achieve a given separation and thus the lower the operating cost of the separation system. The higher the flux, the smaller the membrane area is required thus, the lower the capital cost of the system.

Table 1 summarizes the features of polymeric and inorganic membranes in terms of their technical advantages and disadvantages, and the current status of development [6]. In general, inorganic membranes favor applications under harsh temperature and chemical conditions, whereas polymeric ones have the advantages of being economical.

1.3.2. H₂ separation membranes

Gas separation using polymeric membranes was first reported over 180 years ago by Mitchell in a study with hydrogen and carbon dioxide mixture [7]. In 1866, Graham [8] made the next important step in understanding the permeation process. He proposed that permeation involves a solution-diffusion mechanism by which permeate molecules first dissolved in the upstream face of the membrane were then transported through it by the same process as that occurring in the diffusion of liquids. The first successful application of membrane gas-separation systems came much later (in the 1970's) and it was for hydrogen separation by polymeric membranes from ammonia purge gas streams, and to adjust the hydrogen/carbon monoxide ratio in synthesis gas [9].

Hydrogen separations from highly supercritical gases, such as methane, carbon monoxide, and nitrogen are easy to achieve by polymeric membranes, because of the extremely high diffusion coefficient of hydrogen relative to all other molecules except helium. Even though solubility factors are not favorable for hydrogen, the diffusion contribution dominates and gives overall high selectivities. For example, the hydrogen/methane selectivity of some of the new rigid polyimide and polyamide membranes is about 200. An example of Monsanto's use of membranes for synthesis gas composition adjustment is the

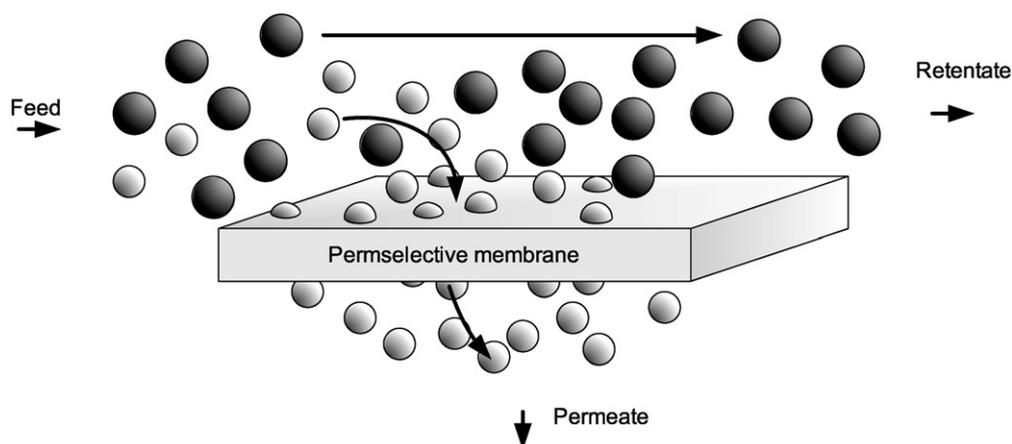


Fig. 1. Simplified concept schematic of membrane separation. Permeability is typically used to indicate the capacity of a membrane for processing the permeate. High permeability means a high throughput. Permeability denotes the flux of mass through a membrane per unit of area and time at a given pressure gradient with several units commonly used: barrer ($10^{-10} \text{ cm}^3(\text{STP}) \text{ cm s}^{-1} \text{ cm}^{-2} \text{ cmHg}^{-1}$), or gas permeation units ($\text{GPU} = 10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$), or molar permeability ($\text{mol m s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$). Permeance is defined as flux per transmembrane driving force ($\text{mol s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$). Selectivity is a membrane's ability to separate a desired component from the feed mixture. Selectivity is often calculated as permselectivity (ratio of permeation of single gases) or as a separation factor α for a mixture.

Table 1
Comparison of polymeric and inorganic membranes

Membrane	Advantages	Disadvantages	Current status
Inorganic	<ul style="list-style-type: none"> • Long term durability • High thermal stability (>200 °C) • Chemical stability in wide pH • High structural integrity 	<ul style="list-style-type: none"> • Brittle (Pd) • Expensive • Some have low hydrothermal stability 	<ul style="list-style-type: none"> • Small scale applications • Surface modifications to improve hydrothermal stability
Polymeric	<ul style="list-style-type: none"> • Cheap • Mass production (larger scale) • Good quality control 	<ul style="list-style-type: none"> • Structurally weak, not stable, temp. limited • Prone to denature & be contaminated (short life) 	<ul style="list-style-type: none"> • Wide applications in aqueous phase, and some gas separations

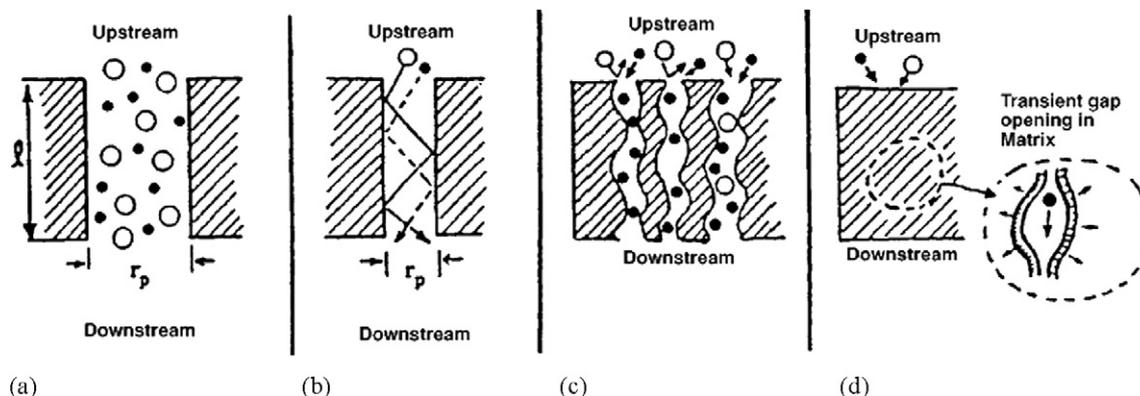


Fig. 2. Various gas separation mechanisms [12] (a) viscous flow, (b) Knudsen diffusion, (c) molecular sieving and (d) solution diffusion.

production of methanol from synthesis gas. Monsanto has published a study of a plant in Texas City producing 100 million gal/yr of methanol [10].

Although polymeric membranes have been used for hydrogen separation in industries, particularly for low temperature applications for many years [11], the high temperature stability problem limits the applications of these membranes to membrane reactors for hydrogen production. In this article, we focus our review on the inorganic membranes systems for hydrogen separation and for membrane reactors involving the removal of hydrogen. Hydrogen-permselective inorganic membranes are further classified into three main groups: (i) microporous ceramic or molecular sieves, (ii) dense-phase metal or metal alloys, and (iii) dense ceramic perovskites. The former follows the activated diffusion mechanism, and the latter solution-diffusion, as illustrated in Fig. 2.

There are generally four molecular transport mechanism through membranes as summarized below:

- (a) Viscous flow, no separation is achieved.
 (b) Knudsen flow regime, separation is based on the inverse square root ratio of the molecular weights of A and B (when the pore radius is smaller than the gas molecule's mean free path); separation factor:

$$\alpha_{AB} = \left[\frac{M_B}{M_A} \right]^{1/2}.$$

- (c) Micropore molecular sieving (or activated diffusion), separation is based on the much higher diffusion rates of the smallest molecule, but adsorption capacities may be impor-

tant factors for similarly sized molecules such as O₂ and N₂.

- (d) Solution-diffusion regime, separation is based on both solubility and mobility factors in essentially all cases, especially for non-porous polymeric membranes. Diffusivity selectivity favors the smallest molecule. Solubility selectivity favors the most condensable molecule. The concept of transient gap opening does not apply to the process of hydrogen permeation through a dense-phase metallic membrane. Although the transport mechanism of hydrogen through metallic membranes is also solution-diffusion, the process is much more complex than in polymeric films, which will be discussed in Section 1.3.3 in more detail.

1.3.3. Important membrane properties required for efficient separation

As mentioned earlier, the basic and important properties are selectivity and permeability. In the absence of defects, the selectivity is a function of the material properties at given operating conditions. The productivity is a function of the material properties as well as the thickness of the membrane film, and the lower the thickness, the higher the productivity. According to Koros [9], there are two basic requirements for membrane gas separation systems, i.e., technical and practical requirements. The former refers to those characteristics that must be present for the system to even be considered for the application. The latter refers to the characteristics important in making a technically acceptable system competitive with alternative technologies, such as cryogenic distillation or pressure-swing adsorption (PSA). The *technical requirements* for two main types of membranes of interest to hydrogen separation are as follows:

- (1) For solution-diffusion membranes (polymeric or metallic), it is critical to attain a perfect pin-hole free or crack-free selective layer that can last for the entire working life of the membrane in the presence of system upsets and long-term pressurization.
- (2) For molecular-sieve membranes, a similar standard of perfection must be ensured to have no continuous pores with sizes greater than a certain critical size existing between the upstream and downstream membrane faces. For hydrogen separation, the pore size limit is around 0.3–0.4 nm [13,14]. Adsorption on the pore walls may reduce the effective openings well below that of the “dry” substrate.
- (3) Most gas streams in industry contain condensable and adsorptive or even reactive components, so it is often desirable to remove such components prior to the membrane separation stage. Such pretreatment is not a major problem and other competitive separation processes such as PSA also use feed pretreatments. However, the more robust the membrane system is in its ability to accept unconditioned feeds, the more attractive it is in terms of flexibility and ease of operation. Therefore, for any type of membranes the chemical stability and/or thermal stability are of significant concern with respect to its life and operation.

Besides the technical requirements as mentioned above, *practical requirements* dictate that a membrane should provide commercially attractive throughputs (fluxes). Even for materials with relatively high intrinsic permeabilities, commercially viable fluxes require that the effective thickness of the membrane be made as small as possible without introducing defects that destroy the intrinsic selectivity of the material. In practice, even highly permeable membranes are not used in thick film form to minimize the total materials costs because of the enormous membrane areas required for large-scale gas separation.

In addition to flux, a practical membrane system must be able to achieve certain upstream or downstream gas (hydrogen) compositions. The *ideal separation factor or permselectivity*, i.e., the ratio of the intrinsic permeabilities of the two permeates, should be as high as possible to allow flexibility in setting transmembrane pressure differences, while still meeting gas purity requirements. Permselectivity also determines the energy used in compressing the feed gas, and if multistage system designs are needed. Unfortunately, high permselectivities often correlate with low intrinsic membrane permeabilities, and this presents a compromise between productivity and selectivity of the membrane. The trade-off between intrinsic membrane permeability and selectivity is a major issue concerning researchers who are constantly striving for better materials to optimize both properties.

2. Dense phase membranes

Dense phase metallic and metallic alloy membranes have attracted a great deal of attention largely because they are commercially available. These membranes exist in a variety of compositions and can be made into large-scale continuous films for membrane module assemblies. For hydrogen, so far there has

been some limited number of metallic membranes available that are effective. These are primarily palladium (Pd)-based alloys exhibiting unique permselectivity to hydrogen and generally good mechanical stability [15–20]. Originally used in the form of relatively thick dense metal membranes, the self-supporting thick membranes (50–100 μm) have been found unattractive because of the high costs, low permeance and low chemical stability. Instead, current Pd-based membranes consists of a thin layer (<20 μm) of the palladium or palladium alloy deposited onto a porous ceramic or metal substrate [3,21–23]. The alloying elements are believed to improve the membrane's resistance to hydrogen embrittlement [24] and increase hydrogen permeance [25]. For example, in PdAg, the most commonly used alloy for hydrogen extraction, the hydrogen permeability increased with silver content to reach a maximum at around 23 wt% Ag. Alloying Pd with Ag decreases the diffusivity but this is compensated for by an increase in hydrogen solubility. Such alloyed membranes have good stability and lower material costs, offering higher hydrogen fluxes and better mechanical properties than thicker metal membranes.

2.1. Preparation and characterization of metal-based membranes

Generally there are three techniques for coating metallic thin films onto porous metallic or ceramic supports: *electroless plating*, *chemical vapor deposition (CVD)* and *physical sputtering*. Under controlled conditions all three methods produce good quality membranes with high hydrogen selectivity over 3000 at temperatures above 300 °C. Most of the work on preparation of Pd-based membranes was conducted in the 1990s, for instance, on electroless plating technique [3,26,27], chemical vapor deposition [23,28], magnetron sputtering [29–31] and spray pyrolysis [24].

The electroless plating technique is a simpler and often more effective method of preparation which has a number of advantages such as uniformity of coatings on complex shapes, high coating adhesion, low cost, equipment and operation simplicity. The CVD method also has the advantages of ease to scale up and flexibility to coat metal film on support of different geometry. The main disadvantage of these two chemical methods is the difficulty to control the composition of metal alloy deposited.

DC or RF sputtering method of depositing Pd and its alloys, however, is found to produce very thin Pd/Ag membranes of good quality [31]. Lin's group deposited metal membranes inside the mesopores of alumina support in order to circumvent mechanical problem associated with alpha-beta phase transformation due to hydrogen pressure and temperature changes [28]. However, the metal membrane formed by deposits in the pores exhibited a lower hydrogen permeance as compared to the metal film on the support surface. Alloying a second metal with Pd is an effective way to avoid the phase transformation (hydrogen embrittlement).

In electroless plating of Pd films, Pd particles are normally produced by reduction of the plating solution containing amine–Pd complexes. These particles then grow on Pd nuclei

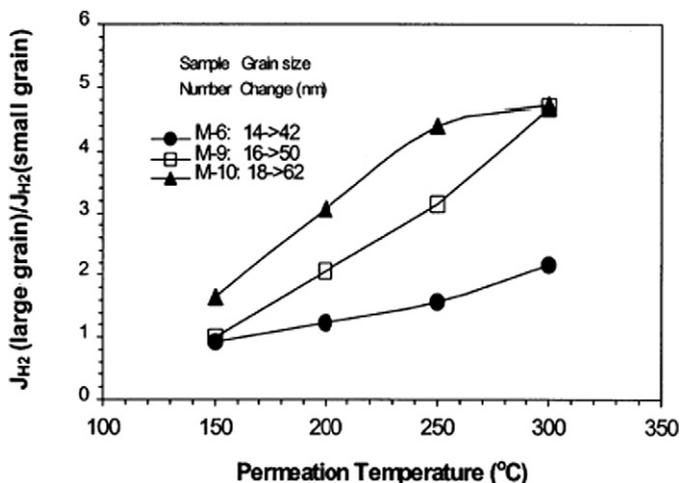


Fig. 3. Ratio of hydrogen permeance after grain growth to that before the grain growth for three different nanocrystalline Pd–Ag membranes of about 200 nm in thickness prepared by sputtering method [36].

seeded on the substrate through a successive activation and sensitization processes, which is autocatalysed by the Pd particles. Despite its inherent simplicity, defects in the Pd layer can develop due to impurities in the plating solution. On the other hand, rapid temperature change may also lead to the formation of defects caused by the different thermal expansion coefficients of Pd (or its alloy) and the substrate.

A new electroless plating technique combining the conventional plating with osmosis was further developed by Yeung and co-workers [32–34]. By this method, the initial loose structure of the deposited Pd could be densified as a result of the migration of Pd to the vicinity of the defects. In the recent study, Li et al. [35] used this new method to repair Pd/ α -Al₂O₃ composite membranes, which originally contained a large number of defects.

In terms of the microstructure of the thin films produced, the following summarizes the different features of the products by three different methods [36]:

- Thin Pd/Ag membranes prepared by the electroless plating tend to contain large crystallites (in submicron range).
- The CVD metal membranes can be polycrystalline or nanocrystalline depending on the deposition conditions in 100 s nm.
- Those by the sputtering deposition are nanocrystalline with crystallite sizes in the range of 20–100 nm.

There are many discrepancies in the literature on hydrogen permeation data through various thin Pd/Ag membranes prepared by different methods [37]. These discrepancies cannot be explained by the differences in membrane thickness and composition. The effects of the microstructure (e.g., the crystallite size) on hydrogen permeation could be important.

To examine the effects of the grain size on hydrogen permeation, Lin and co-workers [36] prepared submicron-thick, nanocrystalline Pd/Ag films by sputtering method. The films were annealed at 600 °C for grain growth. The hydrogen permeation through the membrane was measured before and after

the grain grown. Fig. 3 shows the grain sizes before and after the annealing, and the ratio of the hydrogen permeance for Pd/Ag membrane after the grain growth (with larger size) to that before the grain growth (with smaller size) at different permeation temperatures. It is shown that an increase in grain (crystallite) size results in higher hydrogen permeance, with more significant enhancement at higher permeation temperatures. These data clearly indicate the importance of nanostructure (thus deposition method) of the Pd–Ag film on hydrogen permeance.

2.2. Hydrogen permeation in dense metal membranes

The permeation of hydrogen through a metallic (such as Pd) film is a complex process. The process involves sorption of hydrogen molecules on the film surface and desorption from the ceramic substrate. The hydrogen molecule dissociates into hydrogen atoms on the feed side of the film, then diffuse through the film and re-associate on the permeate side. Since the dissociation reaction kinetics hydrogen and the reverse reaction are relatively fast, the diffusion of hydrogen atoms through the metal film is generally the rate-limiting step. The permeability can be considered as product of solubility and diffusivity. The permeation rate of hydrogen can be given by [29]:

$$J_A = \frac{\varepsilon_A}{l} [(P_f x_A)^n - (P_p y_A)^n], \quad (3)$$

$$\varepsilon_A = D_0 S \exp\left(-\frac{E_p}{RT}\right), \quad (4)$$

where J_A is the rate of more permeable species A ($\text{mol m}^{-2} \text{s}^{-1}$), l is the membrane thickness (m), P_f is the feed-side pressure and P_p permeate-side pressure (kPa), ε_A is the membrane permeability of more permeable component A ($\text{mol m m}^{-2} \text{s}^{-1} \text{kPa}^{-n}$), D_0 is the diffusivity of hydrogen ($\text{m}^2 \text{s}^{-1}$), S is the hydrogen solubility in metal film (mol m^{-3}), E_p is the activation energy for permeation (equal to the sum of the diffusion energy and the heat of dissolution) (kJ mol^{-1}), x is the mole fraction in feed side (a being more permeable) and y mole fraction in permeate side.

If diffusion through the metal film is the rate-limiting step and hydrogen atoms form an ideal solution in the metal, then Sievert's law [38] holds and n is equal to 0.5. The hydrogen flux is inversely proportional to the membrane metal film thickness (l). In the case of polymeric membrane where selective transport of a gas is by a solution-diffusion process, the exponent n in Eq. (3) is always unity.

Hydrogen flux depends on both the membrane materials and the thickness of the selective layer. The permeation conditions such as pressure and temperature affect the flux according to Eq. (1). For example, Jarosch and de Lasa [41] reported a study on hydrogen permeation in thick film Pd membranes supported on Inconel porous substrate (500 nm diameter) for steam reforming membrane reactor application. They observed typical H₂ permeabilities of $1.874 \times 10^{-6} \text{ mol m}^{-1} \text{ s}^{-1} \text{ kPa}^{-0.5}$ with activation energy of 22.6 kJ mol^{-1} . This is compared to the permeability of $1.05 \times 10^{-5} \text{ mol m}^{-1} \text{ s}^{-1} \text{ kPa}^{-0.5}$ reported for a foil-supported thick film of Pd [39], and $8.9 \times 10^{-7} - 2.7 \times 10^{-6}$

for a porous alumina supported thin Pd membrane (17 μm) in the temperature range of 450–600 $^{\circ}\text{C}$ [40]. The highest permeability reported is 2.0×10^{-5} for S316L supported Pd membrane of about 20 μm [3] in similar temperature range. Clearly, there is wide variation in the values reported for the permeability data depending on the substrate, coating methods used. Generally, the permeabilities of Pd supported membranes follow the order: Electroless deposition > CVD deposition > sputtering method.

Membranes produced by the electroless technique exhibited hydrogen/argon molar selectivities in the range of 336–1187. The temperature dependence of the permeance followed Sievert's law, which indicated a film-diffusion rate-limiting mechanism.

Selectivity. In theory, a Pd membrane free of defects should have an infinite selectivity for hydrogen over any other species. In practice, most thin films contain some degree of defects such as pinholes or pores. Depending on the environment to which the membrane is exposed, cracks and pinholes can also develop in the film as a result of phase change in the palladium/hydrogen system [28]. For these reasons, the selectivity is often found to have a finite value. In Jarosch's work, the selectivity was found to be increasing with temperature (Fig. 5), and decreasing with increasing differential hydrogen partial pressure. This is obviously due to a combination of bulk hydrogen diffusion through the Pd film and Knudsen diffusion of hydrogen and argon through the pores of the substrate. For a given differential hydrogen pressure, the rate of hydrogen diffusion through the Pd film increases with temperature, whereas the rate of Knudsen diffusion decreases. For a given temperature, the selectivity falls with increasing differential hydrogen partial pressure because hydrogen diffusion through bulk palladium is proportional (Eq. (3)) to the difference in the square root of the hydrogen partial pressures on the two sides of the membrane whereas Knudsen diffusion through the pores is directly proportional to the partial pressure difference.

The selectivity values obtained by Jarosch and de Lasa are comparable to those reported in the literature. Li et al. [42] found that the selectivity for hydrogen over nitrogen for a composite palladium/stainless steel (316L) membrane produced by electroless deposition ranged from 400 to 1600 over the temperature range 325–475 $^{\circ}\text{C}$. Nam et al. [43] reported hydrogen/nitrogen selectivities between 500 and 4700 over the temperature range 350–500 $^{\circ}\text{C}$ for composite palladium/stainless steel membranes.

Uemiyama et al. [44] reported the results of the H_2 permeation tests for the supported non-Pd membranes in comparison with Pd membrane. Fig. 6 gives a good comparison of various metallic membranes prepared by CVD method in the form of Arrhenius plots. It is seen that the hydrogen flux for Pd membrane is higher than other metals. The permeability for Pd supported membrane is in the order $1 \times 10^{-7} \text{ mol m}^{-1} \text{ s}^{-1} \text{ kPa}^{-0.5}$ at 750 $^{\circ}\text{C}$. This shows that the supported Pd membranes prepared by CVD method has considerably lower permeabilities than those prepared by electroless deposition.

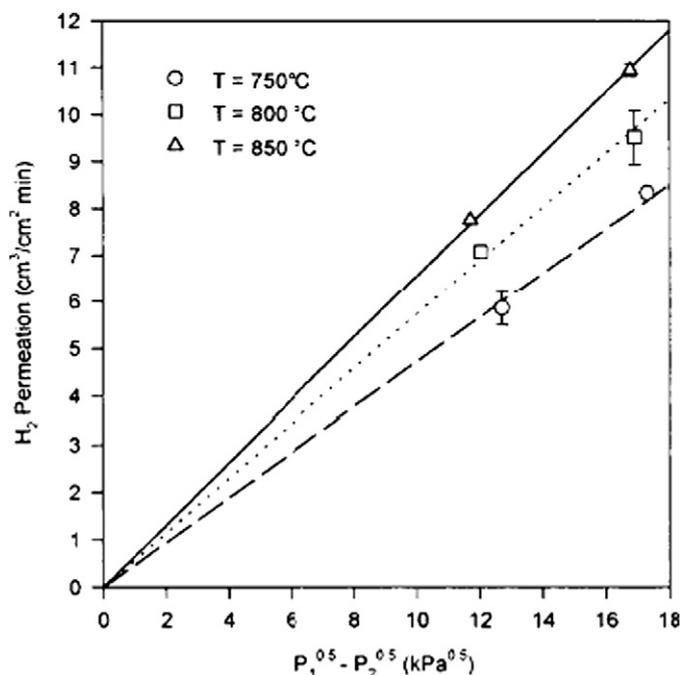


Fig. 4. Hydrogen permeance as a function of the difference between the square roots of the hydrogen partial pressures on the retentate and permeate sides for an electroless deposited thick film membrane (156 μm) [41].

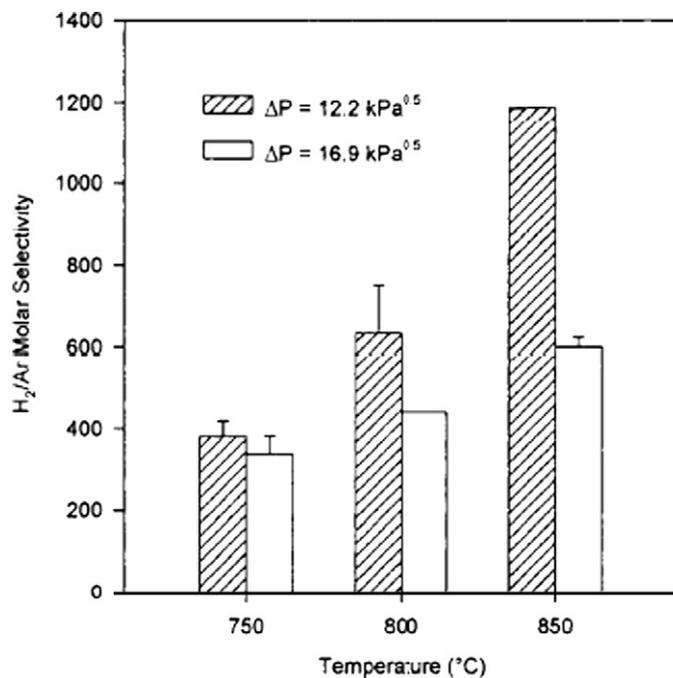


Fig. 5. Selectivity of hydrogen over argon for an electroless deposited thick film membrane (156 μm) [41].

2.3. Critical issues in dense-phase membranes

In general, dense phase metallic or alloy membranes (with Pd being the best precious metal for high permeability), offer very high selectivity for hydrogen practically in the order of 10^3 . The permeance of hydrogen with thick self-supporting Pd membranes tends to be higher than supported thin film mem-

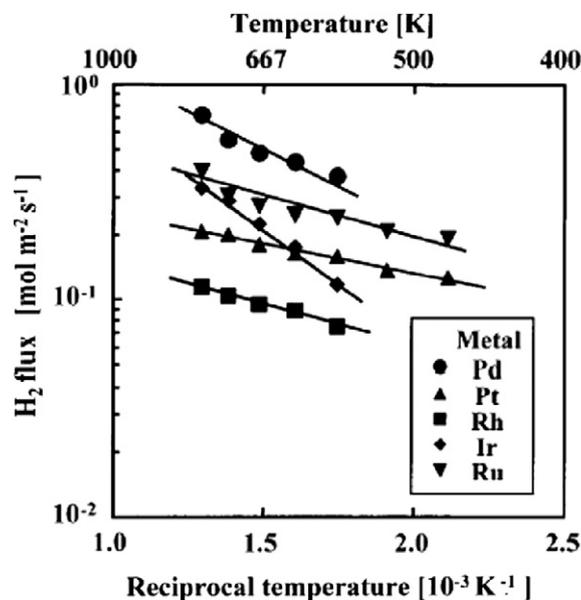


Fig. 6. Comparison of hydrogen flux for various supported metal membranes prepared by CVD ($\Delta P = 196$ kPa; thickness Pd 3.3 μm , Ru 3.2 μm , Pt 5.8 μm , Rh 17.3 μm , Ir 8.3 μm) [44].

branes, primarily because the very large grain size in these films. Electroless deposited Pd or Pd-alloy membranes have higher permeability than those prepared by other methods.

However, Pd membranes can undergo phase transformation which lead to cracks in the metal film due to expansion of the metal lattice. These phase changes are very pressure and temperature dependent. In the 1960s commercially manufactured Pd diffusers were used to extract H_2 from waste process gas streams, but within one year of their operation, pinholes and cracks developed and thus the operation was terminated [45]. Mordkovich et al. [17] claimed a successful application of multimetallic Pd membrane with high resistance to phase change and cracking in pilot plant study. Four membrane columns, each 10 m long were used for two years for the hydrogen recovery from an NH_3 purge gas to produce pure H_2 at 30 atm with 96% H_2 purity (feed at 200 atm). However, no independent verification or confirmation is found in the literature for similar success in large-scale applications. In order to minimize operational problems, the current research effort focus is on deposition of Pd alloys to mesoporous supports. Relatively thicker films are required to minimize defects, so flux is limited. Other means to tackle the Pd embrittlement issue includes use of low cost amorphous alloys such as Zr, Ni, Cu and Al, but being a more recent technology is still in need of development toward practical operation [46]. It has also been reported that Pd-based membranes are prone to be poisoned by impurity gases such as H_2S , CO and deposition of carbonaceous species during the application [35,47].

Another problem associated with the metal membranes is the deposition of carbonaceous impurities when an initially defect free palladium composite membrane is used in high temperature catalytic applications. The further diffusion of these deposited carbonaceous impurities into the bulk phase of the membrane can lead to defects in the membrane [48]. This is

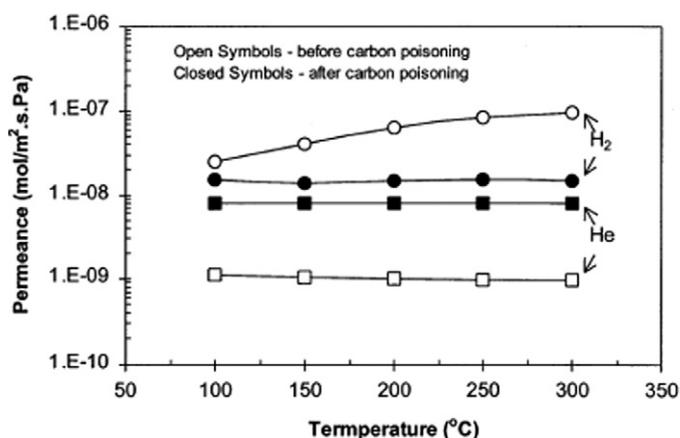


Fig. 7. Hydrogen and helium permeance (with the feed of 1:1 hydrogen and helium mixture) through a 200 nm thick Pd/Ag membrane before and after being exposed to a carbon source at 600 $^{\circ}\text{C}$ [36].

more significant to thin-film membranes. Lin et al. [36] have conducted some systematic investigations on this aspect. Fig. 7 shows permeance and separation results of a thin Pd/Ag membrane prepared by sputter deposition before and after being exposed to a graphite ring (surrounding the membrane disk) at 600 $^{\circ}\text{C}$ overnight. XRD analysis shows expansion of Pd/Ag lattice, indicating carbon diffusion into the lattice after exposing the Pd/Ag membrane to the carbon-containing source. The increase in helium permeance after poisoning indicates a change of the Pd/Ag membrane microstructure after the expansion of Pd/Ag lattice, creating defects or enlarging the grain-boundary. The incorporation of carbon in Pd/Ag lattice could reduce hydrogen solubility, decreasing the hydrogen permeability of the membrane. Re-exposure of the poisoned Pd/Ag to hydrogen atmosphere could remove the poisoning agent but cannot restore the mechanical integrity of Pd/Ag membrane that was destroyed by the poisoning.

The following summarizes the main limitations of Pd-based membranes for hydrogen separation. Use of Pd membranes must be balanced against these demonstrated limitations [45]:

- Best membranes have limited life (months) mainly due to cracking or pinhole formation. Since pure H_2 is desired, this is unacceptable and must be improved.
- Membranes must be operated above 250 $^{\circ}\text{C}$ when CO is present.
- Alloys of Pd can undergo surface enrichment of the minor metal atoms during long term operation.
- Sensitivity of Pd to traces of iron, which causes pinholes (this can be minimized by using aluminized steel for piping ahead of the membrane).
- Need for ultra thin, continuous layers of Pd in order to maximize H_2 flux.
- Low surface area of metals requires complex membrane reactor designs to maximize surface to volume ratio.
- Pd is a precious, commodity metal whose prices vary with unpredictable market forces.

3. Microporous inorganic membranes

Porous ceramic, particularly microporous membranes possess high permeability and moderate to high selectivity, and are chemically and thermally stable. Therefore, they are attractive for applications in hydrogen production reactions. There are various types of porous membranes that have been tested for hydrogen separation or production in the literature. These include carbon molecular sieve membranes [49] for refinery gas separation and hydrogen recovery. They have demonstrated in pilot scale studies that carbon molecular sieve membranes can be very efficient for separating H_2 from refinery gas streams. Air products and chemicals Inc. has employed such technology for hydrogen enrichment to 56–60% prior to PSA purification to produce 99.99% H_2 [45]. However, due to its complex surface chemistry carbon molecular sieves are not considered to be feasible candidates for membrane reactor applications such as in steam reforming and the water gas shift reactions because of the oxidative nature of its surface. Another type of porous ceramic membrane reported for use in H_2 production application is based on alumina mesoporous membranes [50]. However, most of the separation data were for helium and carbon tetrafluoride, not for hydrogen. Even for He, the selectivity is fairly low around the Knudsen separation factor in the order of 1–10.

Silica and silica functionalized ceramic membranes are showing great potential for intended application of hydrogen separation and production. There has been a large development in silica membranes in the last decade with several groups in the USA, Holland, Germany, Japan and Australia leading the research efforts in this area. The following subsection will present an overview of microporous molecular sieve membranes based on sol–gel derived silica materials which have been reported to be good hydrogen permselective membranes.

3.1. Preparation and permeation properties

Molecular sieve silica (MSS) membranes are a class of microporous membranes derived by sol–gel technique. Fig. 8 shows a schematic of the sol–gel preparation process of MSS membranes. The sol–gel method is divided into two routes, the colloidal suspension route and the polymeric gel route. In both methods, the precursor is used hydrolyzed followed by further condensation. The use of template agents enables the pore size tailoring towards molecular size for intermediate or top selective layers. These include organic covalently bonded templates such as methyl groups [51–53] and non-covalently bonded or-

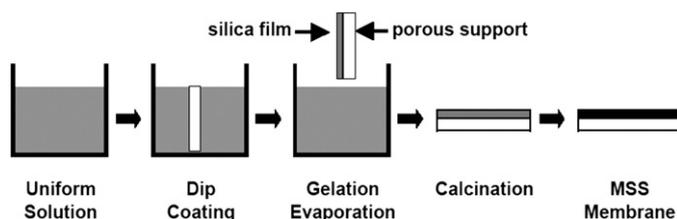


Fig. 8. Schematic process of sol–gel method for preparing MSS membranes.

ganic templates such as C_6 - and C_{16} -surfactants [54–56] and alkyl-tri-ethoxy-silanes [57].

3.1.1. Colloidal suspension route

In this method a colloidal suspension, consisting of a particle and agglomerate chain network is formed by a hydrolysis step using an excess of water. The technique is to make silica particles of different sizes and then to coat progressively the smaller silica particles onto the support or underlying layers with bigger pore size. The sols are prepared by the acid catalysed hydrolysis of tetra-ethyl-ortho-silicate (TEOS) [58]. The resulting pore size distribution (PSD) is generally mesoporous. Even so, Tsuru et al. [59] claimed that pore sizes of 3–4 Å could be achieved by the colloidal method. Naito et al. [58] modified α -alumina supports with colloidal silica sols by emphasizing the importance of parameters controlling the dip coating process. Of particular attention, the number of layers and the order in which the various sols are dip coated is important for the resulting pore size. This is mainly due to the dispersion medium during the dip coating process, which is forced into the pores of the underlying layer by capillary action of the microporous matrices.

Fast hydrolysis, slow condensation, and low solubility achieved by acid reaction conditions all contribute to a high supersaturation level and result in small particles. Alkoxy-silicates have small alkyl groups, which react faster with water leading to smaller particles. These observations were reported by Chu et al. [60] who prepared colloidal silica particles from alkyl silicates such as tetra-methyl-ortho-silicate (TMOS), tetra-ethyl-ortho-silicate (TEOS).

3.1.2. Polymeric sol–gel route

The standard sol–gel process is controlled by hydrolysis and condensation reactions [61]. Various research groups have produced high quality membranes using a single-step catalyzed hydrolysis [14,62] or a two-step catalyzed hydrolysis sol–gel process [13,54–56]. The catalyzed hydrolysis process employs the use of tetra-ethyl-ortho-silicate (TEOS) precursors mixed with ethanol (EtOH), an acid catalyst (HCl or HNO_3) and distilled water. Diniz da Costa et al. [13] have reported that sol–gel derived films with a large contribution of silanol groups (SiOH) prepared by the two-step sol gel process have much smaller pore sizes with molecular dimensions in the region of 3–4 Å than those with a large contribution of siloxane bonds (SiO_4) prepared by the single-step sol–gel process. Hence, these materials are ideal precursors to synthesize membranes with the molecular dimensions required to separate a large gas molecule from a small one.

Brinker and Scherer [63] extensively reviewed the sol–gel process and its science. Depending on the pH and the $H_2O:Si$ molar ratio ($r < 5$), only weakly branched networks are formed. In this case there is a tendency for structures to interpenetrate forming micropore apertures of molecular size. The hydrolysis and condensation reactions in the sol–gel process lead to the growth and aggregation of clusters resulting in gel formation. The film microstructure depends upon the preceding formulation and preparation procedures of sols to the gel point, as well as the preceding aging, drying, and heat treatment of

the gels. During heat treatment continuing condensation reactions lead to the strengthening of the network due to polymeric crosslinking. Buckley and Greenblatt [64] investigated the pore characteristics of xerogels prepared with TEOS, ethanol and water. They found that by increasing the ethanol content of the solution, the particle size decreased. They also reported that increasing the alkyl chain of the alcohol solvent, the xerogel structure changed from microporous to mesoporous. In addition, they showed that low water content favored mesoporosity, whereas high water content favored macroporosity.

An important technique to tailor the pore size of intermediate or top layers of membranes is to add organic template agents during the sol–gel process. This field has been reviewed by Raman et al. [65]. Baker et al. [66] explored the potential of xerogel composites by investigating various organic oligomers and surfactants as possible modifying agents. The incorporation of organic components within the sol–gel process leads to composites that can help to produce crack-free materials and improve coating–substrate adhesion. There are two classes of sol–gel composites derived from template agents. The first one is a covalently bonded organic template, such as methyl groups (CH₃) in methyltriethoxysilane (MTES), which has a co-monomer non-hydrolysalable functionality. The second method employs a non-covalently organic oligomer or surfactant which interact with the sol by weak van der Waals, hydrogen or ionic bonds, or hydrophilic–hydrophobic routes.

3.2. Performance in hydrogen permeation

For gas diffusion in molecular sieve membranes, differences in permeability of gases with different kinetic diameters exceed the differences in polymeric membranes. This was noted first by Shelekhin et al. [67] who plotted the permeance against the kinetic diameter of gases. Using the proposed method of diffusion by Shelekhin and co-workers, the upper bound for the permeability the molecular sieve membrane was estimated to be $30,000 \times 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm s}^{-1} \text{ cm}^{-2} \text{ cmHg}^{-1}$ (barrers). An upper bound for H₂ selective membranes from the literature is shown in Fig. 9. To obtain this upper bound, the separation factor versus permeability is plotted as log–log data, so that the equation $\varepsilon = k\alpha^n$ can be used. The low region of permeabilities and selectivities is bound by polymeric membranes, whereas inorganic microporous membranes lie in the high permeabilities and selectivities region.

The diffusion of molecules in ultramicroporous ($d_p < 5 \text{ \AA}$) materials can be modeled as an activated transport mechanism. Contrary to Knudsen diffusion, Poiseuille flow or surface diffusion, activated transport is mainly characterized by an increase in permeation as a function of temperature. Monoatomic and diatomic gases will generally comply with activated transport for high quality ultramicroporous membranes, whereas hydrocarbon permeation will decrease with temperature, as surface diffusion will be the main transport mechanism. The activated transport mechanism was firstly derived by Barrer [68] for intercrystalline diffusion of molecules. In the case ultramicroporous silica membranes, microporous flux is rate determining as the

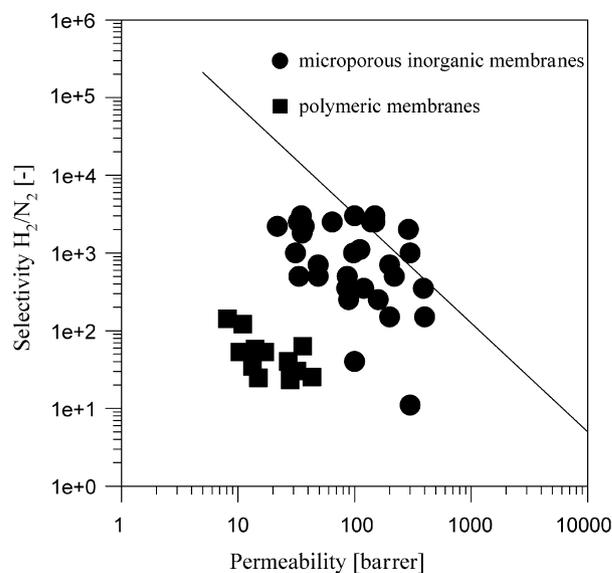


Fig. 9. Literature data for H₂/N₂ separation factor versus H₂ permeability for microporous membranes.

contribution of external surface flux is not significant. Hence, the activation energy (E_A) for permeation of gases is determined by:

$$E_A = E_m - Q_{st}, \quad (5)$$

where Q_{st} is the isosteric heat of adsorption and E_m is the energy of mobility required for molecules to jump from one site to another inside the micropore. Apart from permeation and permselectivity, Burggraaf indicated that the activation energy (E_A) for permeation of gases could be considered as a further quality index for the membrane. High quality molecular sieve silica membranes generally have activation energies for the H₂ permeance in excess of 10 kJ mol^{-1} . In other words, high activation energy gives an indication that the permeation increases at a higher rate with temperature than a membrane with smaller activation energy. This is attributable to a high value of E_m from the presence of highly selective tight pore spaces.

In a membrane system, the transport mechanisms change from activated transport for the microporous top layer to Knudsen diffusion and Poiseuille permeation for support (mesoporous and macroporous materials). Hence, the transport resistance of the support has to be taken into account to calculate E_A . The resistance can be derived from analogous resistance circuits although it is generally observed that the top layer limits the diffusion (i.e., rate determining). Q_{st} and E_m can be determined through the van't Hoff relation (Eq. (6)) and the Arrhenius relation (Eq. (7)), respectively.

$$K = K_0 \exp\left(\frac{Q_{st}}{RT}\right), \quad (6)$$

$$D = D_0 \exp\left(-\frac{E_m}{RT}\right). \quad (7)$$

Common precursors for the CVD process are TEOS, phenyltriethoxysilane (PTES) or di-phenyl-diethoxysilane (DPDES). The supports used are mostly Vycor glass or α - and γ -alumina.

Table 2
Comparison of H₂ selective silica membranes derived by different methods

Type of membrane	H ₂ permeance ($\times 10^{-8}$ mol m ⁻² s ⁻¹ Pa ⁻¹)	Selectivity	Hydrothermal stability	Reference
CVD TEOS	0.89–9.8	>1000 H ₂ /N ₂	7% moisture no degradation	Yan et al. [69]
CVD TEOS	2	10–230 H ₂ /N ₂		Hwang et al. [70]
CVD TEOS	5	1250 H ₂ /N ₂	H ₂ /N ₂ dropped to 800 after 15 h	Nomura et al. [71]
CVD SiO ₂	0.34–2	12–72 H ₂ /N ₂	Flux 60% lower	Wu et al. [72]
CVD SiO ₂	2	30–1500	increased hydrophob.	Tsapatsis [73]
Colloidal silica	130	70 H ₂ /CO ₂		Naito et al. [58]
Sol–gel TEOS	200	40–200 H ₂ /CH ₄		de Vos and Verweij [14]
Sol–gel TEOS	150	9–15 H ₂ /CO ₂	–	de Lange et al. [62]
Sol–gel TEOS and alkyltriethoxysilanes	10	1265 H ₂ /CH ₄		Kusakabe et al. [57]
Sol–gel	100	15 H ₂ /N ₂		Collins et al. [74]
Sol–gel (two-step)	2	24 H ₂ /CO	Stable over 200 h	Duke et al. [56]

The most recent properties achieved for CVD derived silica membranes are reported by Nomura et al. [71] and Tsapatsis et al. [73]. On average the achievable selectivity factor for H₂/N₂ is between 30–1500 whereas the permeability is around 2×10^{-8} mol m⁻² s⁻¹ Pa⁻¹ at temperature up to 500 °C. However, CVD synthesized membranes generally result in lower permeabilities than the colloidal or polymeric sol–gel routes membranes if tested at the same temperature as shown in Table 2. Hence, the latter processes are more attractive in producing molecular sieve silica (MSS) membranes with higher (1–2 order higher) permeabilities.

3.3. Critical issues in microporous membranes

Hydrothermal stability of MSS materials is a major concern when applied in gas streams containing water vapor. Water reacts with the hydrophilic sites in the silica thin films resulting in chemical and microstructural instability. Until now the importance of the hydrothermal stability for membranes has been mostly neglected and has only been tested for the supports of microporous membranes such as zirconia, alumina and titania membranes. The interaction of the water molecules with the silica surface depends on the type of the functional groups, which are mainly hydroxyl-groups in the case of the silica.

A prolonged exposure of silica materials to humid air at temperatures higher than the calcination temperature of silica (400 °C) causes rapid densification. Fotou et al. [75] tried to increase the thermal stability by doping the starting silica sol with traces of Al₂O₃ or MgO nitrate salts. They showed that doping with alumina increased the thermal stability up to 600 °C. The increase in the thermal stability of sol–gel derived silica membranes was also achieved by Yoshida et al. [76] with an addition of zirconia. The membranes were tested for H₂ permeation and it was shown that the activation energy increased with increasing content of zirconia, which indicates a densification of these membranes. In addition, the good chemical stability of inorganic microporous silica membranes is advantageous in environments containing hydrogen iodide or hydrogen sulfide. Hwang et al. [70] measured the hydrogen separation through a silica membrane, which showed a permeance

of 6×10^{-9} mol m⁻² Pa⁻¹ s⁻¹ and a selectivity for H₂/N₂ of 5–160 at 600 °C. These membranes showed a good stability in a one-day exposure to a mixture of H₂–H₂O–HI. Similar results were reported for a mixture of H₂–H₂O–HBr. More recently, Duke et al. [56] applied a novel carbonised template into the silica micropores which provided hydrostable operation at 200 °C with no loss to selectivity observed after almost 200 hours of continuous operation. In this material, the carbon moieties acted to inhibit micropore collapse, which occurs normally in microporous silica under hydrothermal conditions [77].

4. State of the art in membrane reactors

Following the work of Gryaznov [16] on membrane reactors using palladium alloys, the use of membranes to increase the conversion of reversible reactions by separating gaseous products has been largely studied by a number of researchers. The results have been summarized in a number of recent reviews [45,78–84]. Some significant advantageous of membrane reactors, compared to conventional reactors are:

- Yield-enhancement of equilibrium limited reactions compared to conventional reactors.
- The reactor and the membrane can be divided into two individual compartments. For some reactions (e.g., oxidative dehydrogenation reaction) this aspect may be very important: by separating the stream and the oxidant, the extent of the side-reactions can be significantly decreased.
- By using a membrane, it is possible to control the interaction between two reactants.
- The stoichiometry of the reaction can be easily maintained.
- The combination of the two processes (catalytic reactor and down-stream separation units) into one unit will reduce capital costs.

A lot of reactions can be carried out in a membrane reactor at lower temperatures compared to the packed bed reactor. Therefore most of the suitable reactions for membrane reactors only demand temperatures between 160–500 °C. As shown before

a lot of silica membranes are capable of working in this temperature range and give a better performance for feed streams containing H_2S or H_2O vapor. In contrast, palladium membranes are easy to poison and the H_2 permeability decreases when the feed contains CO [35], steam or H_2S [85]. This review covers steam reforming and the water gas shift reaction only, although silica membranes have also been reported for dehydrogenation and hydrogenation reactions which have been reviewed by Dixon [84].

4.1. Steam reforming

In the literature, various reports on membrane reactors using porous inorganic membranes and dense membranes are available. Most of the porous membranes reported have a pore diameter of about 4 nm. When comparing the performance of these porous membranes with Palladium membranes, e.g., in a membrane reactor for the steam reforming, dense membranes showed a better performance. The mesoporous membranes have lower permselectivities for H_2/CO_2 and H_2/N_2 than the MSS membranes described in this review because at a pore size of 4 nm activated transport is nonexistent. Yildirim et al., [86] stated that a high hydrogen permselectivity is a key factor in the reactor performance. Criscuoli et al. [87] claimed that the better performance of the palladium membrane with respect to the ceramic one is due not only to the selectivity but also the hydrogen permeation. With the large improvements in membrane materials this difference might be overcome.

Prabhu et al. [88] reviewed hydrogen selective ceramic membranes derived through various synthesis methods. They described the effect of water on the permeability and highlighted a new type of silica membrane prepared by the chemical vapor deposition (CVD) method, which showed 100% selectivity for H_2 with respect to CH_4 , CO and CO_2 . Using this membrane the conversion for the steam reforming could be increased above the equilibrium value. In addition, they emphasized that these membranes have a hydrothermal stability up to 10% H_2O at 600 °C for over 150 h. Prabhu [88] pointed out that the introduction of membrane reactors in an industrial context is still dependent on membrane cost. Therefore, future research directions may be focused on finding new membrane materials with high H_2 permeability and selectivity and manufacturing costs lower than those of palladium [47,87].

For the steam reforming of methane Oklany et al. [85] and Prabhu et al. [88] modeled the behavior of microporous silica membranes in various membrane reactor set-ups. Oklany et al. [85] claimed that Pd/Ag membranes gave better performances than the silica membranes in terms of working parameters such as temperature, pressure, sweep gas ratio and membrane thickness, whereas the performance of the microporous membrane was better when steam has been used as a sweep gas. Gobina [89] mentioned the possibility for microporous silica composite membranes to be applied in coal conversion processes where hydrogen production is required.

Another interesting example is the hydrogen separation membranes used for a new concept for power generation systems: the hydrogen-based turbine system for carbon dioxide

recovery [90]. In the system the natural gas, which contains mainly methane, is reformed; simultaneously the hydrogen is removed from the reforming gas with hydrogen separation membranes (called membrane reformers). These are high temperature inorganic hydrogen separation multi-layer porous ceramic membranes. The residual gas including methane and carbon monoxide is combusted in the after burner with pure oxygen and carbon dioxide is exhausted directly. The methane steam reforming is endothermic and requires temperatures of 900 °C, preventing the possibility of using gas turbine exhaust gas to improve the thermal efficiency of the process. By using the membrane reformer the reaction can be carried out at lower temperatures (450–500 °C) and it might be possible to use the recuperated gas turbine cycle for natural gas.

4.2. Water–gas shift reaction

The water–gas shift (WGS) reaction is a well-known exothermic reaction, with equilibrium constant decreasing with temperature. It is one of the most important industrial reactions that can be used to produce hydrogen for ammonia synthesis, adjust the hydrogen-to-carbon monoxide ratio of synthesis gas and to produce hydrogen from CO from syngas for fuel cell applications. By extracting H_2 from the mixture reaction through the membrane, the reaction is shifted towards the products, thus giving a higher conversion with respect to the equilibrium values.

Giessler et al. [55] compared the performance of MSS membranes in the WGS reaction to Pd-composite membranes used by Basile et al. [91]. The reported composite palladium membrane had a H_2 permeation of $6.25 \times 10^{-8} \text{ mol s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$ and a H_2/N_2 selectivity of 3. Using nitrogen as a sweep gas, the maximum conversion rate for the WGS reaction Basile et al. [91] could obtain was 99.89%. At 300 °C, a molar ratio of CO to H_2O equal to one with an optimum sweep flow, a 94% conversion of CO has been reached by Basile et al. [91]. The MSS membranes of Giessler et al. [55] had H_2/N_2 separation factors of about 35 and H_2 permeances of $2.6 \times 10^{-7} \text{ mol s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$. Under the same conditions used by Basile and co-workers, it was possible to achieve CO conversions of 95% for a feed flow of $100 \text{ cm}^3 \text{ min}^{-1}$ or even 98% for a feed flow of $70 \text{ cm}^3 \text{ min}^{-1}$ with the corresponding optimal sweep flow. These results suggest that the MSS membranes performed slightly better than the Pd-composite membrane.

Giessler and co-workers carried out functionalisation of silica derived membranes for the WGS reaction. They reported that water affects the structure of the silica membranes resulting in pore widening and also pore closure. In Fig. 10a, silica membranes showed that after exposure to steam the flux to both H_2 and CO_2 increase and become non-activated (reduced flux with temperature) while the selectivity decreased from 10 to approximately 1.5. However, functionalisation with surfactants lead to the formation of hydrophobic silica surface resulting in a slight decrease in H_2 and CO_2 permeance, but the selectivity remained constant while activated transport was observed prior and after steam exposure (Fig. 10b). Hence, functionalisation

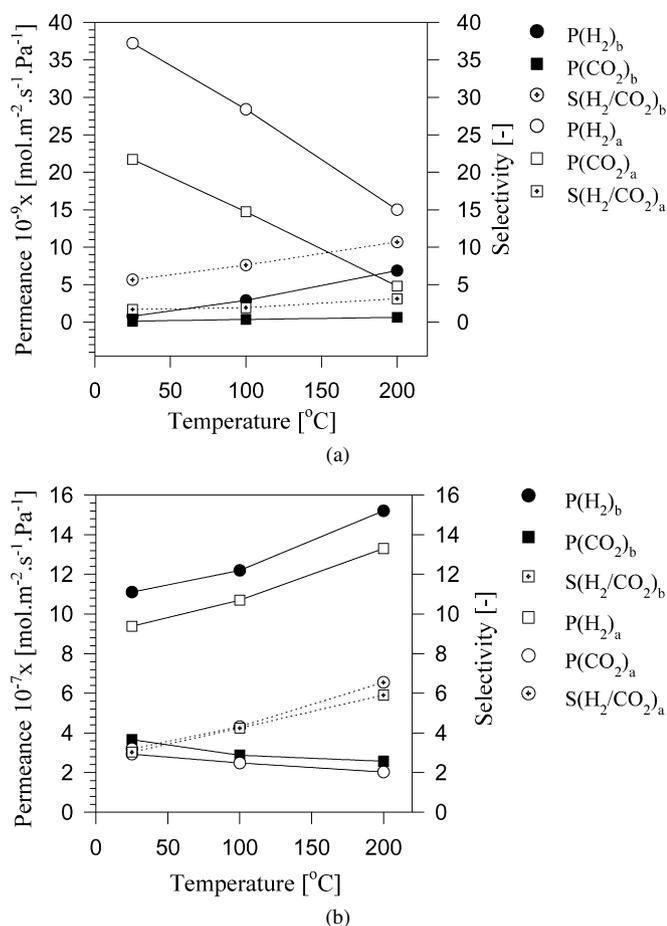


Fig. 10. Temperature dependence performance of (a) hydrophilic membrane and (b) hydrophobic membranes shown as permeation (before)_b and (after)_a exposure to the WGS reaction [55].

allowed robustness to the silica structure under conditions favorable for the water–gas shift (WGS) reaction.

4.3. Further improvements

Another problem still existing in the area of catalytic membrane reactors is the lack of real performance data. In particular data for reaction conditions and the comparison of dense and porous membranes which so far only have been derived by mathematical modeling [35,86,92,93].

Generally, catalytic membrane reactors can be easily integrated with existing plants, and drastic changes are not needed in the process. Although there are a large number of studies on catalytic membrane reactors cited in the literature, a very small number of them are related to the analysis of the costs of these devices. This might be attributed to the fact that the membrane reactor technology is not yet well established and some deficiencies have to be overcome before its implementation at larger scales. Future research should be devoted to the preparation of defect-free and homogeneous membranes able to work for a long period at high temperatures and pressures and even more resistant in aggressive environments; further, higher permeabilities (lower membrane thickness) and selectivities will be needed. The sealing of membranes into modules

is also another point to be improved in order to avoid problems of streams mixing or bypassing during the reaction tests. Finally, the optimization of engineering in module preparation will be a crucial step for increasing the membrane reactor efficiency (higher membrane area per unit volume, developments of systems of control also useful for large scale modules, etc.). These and other aspects related to the development and implementation of membrane reactors are extensively described by Saracco et al. [94,95]. The authors also pointed out that while a lot of progress has been done in the area of film formation and the formation of defect-free membrane films, the areas of high-temperature sealing and scaling-up have been neglected.

A final point of importance relates to the paradox in membrane reactors as pointed out by Dixon [84]. From 1998 to 2002 more than 500 publications appeared in the literature on membrane reactor research, but related industrial applications for large scale projects have not been reported. Many reviews on membrane reactors also support the view that further work is necessary to improve the membrane reactor technology, though its potential for industrial application has been known for decades. Once these problems are solved, the benefits of catalytic membrane reactors in the industrial world could become more realistic. On the other hand, better economic analyses are warranted for stimulating specific technological improvements that need to be made. An economic study [96] for the water–gas shift reaction carried out in an Integrated coal Gasification Combined Cycle (IGCC) system, by using microporous silica membranes, pointed out that more stable and more selective gas separation membranes are necessary in order to have favorable investment and operational costs.

4.4. Concluding remarks and perspective

Inorganic membranes offer advantages such as high flux and high temperature operation, and can be further divided into metallic (dense phase) and ceramic (porous and non-porous). Hydrogen selective membranes come in various types and show differing performance. Metallic Pd types theoretically offer infinite selectivity, but have issues such as precious metals costs and poor thermomechanical stability of the selective film. Ceramic membranes include dense ceramics (perovskites) and microporous, with the latter showing great promise in hydrogen separation thus being the focus of this review.

The key selective molecule transport mechanisms in membranes are solution diffusion for dense and organic types while porous types transport molecules by Knudsen flow and activated diffusion (molecular sieving). The unique hydrogen selective abilities of membranes have significant potential in membrane reactors where constant removal of reaction products could lead to catalyst reductions, reduced operation size, reduced expenses and improved temperature and pressure conditions. Clearly membranes are excellent candidates for hydrogen purification, especially when incorporated with membrane reactor combining reaction/separation in a single unit.

Pd membranes have been researched for well over 50 years with many techniques for manufacturing including the popular electroless plating. The theoretically infinite selectivity to hydrogen continues to draw major research efforts to improve film quality with the reduced thickness necessary to make Pd composite membranes cost effective. Hydrogen embrittlement leads to unstable films solved somewhat by composites with Ag. We believe that Pd composite membranes require further work to improve film stability while remaining cost effective. Pd membrane developments however, are promising with hydrogen to nitrogen selectivities more often around 400–4700, but since CO reduces the membrane's ability to permeate hydrogen below 250 °C, Pd composite membranes may eventually find their place in higher temperature systems, including membrane reactors.

Developments in Molecular Sieve Silica (MSS) membranes in comparison to Pd are far more recent, with membrane selectivity results only appearing around 15 years ago. The ceramic materials are mechanically stable under thermal stresses up to 600 °C, but selectivities are generally lower than Pd, ranging from 9–1500. The two major techniques for manufacturing membranes are sol–gel and chemical vapor deposition (CVD). The sol–gel technique leads to membranes with high permeabilities and good selectivities while the CVD technique leads to good permeabilities and excellent selectivities. The natural reactivity of silica with water has directed researchers to propose material functionalisations making hydrothermally stable membranes. Like Pd membranes, controlling defects and achieving repeatable membrane quality are current topics of concern for MSS membranes.

Hydrogen selective membranes are ideal candidates for membrane reactor and have already been applied showing exciting results. For the water gas shift (WGS) reaction, membrane reactors have the potential to greatly improve the equilibrium limited reaction. Initial investigations showed that both MSS and Pd type membranes can improve conversions above equilibrium, with MSS shown slightly better results when modified for stability in steam.

We can offer the following perspective on hydrogen membranes based on this review:

- Scale up of hydrogen membrane technologies is the most challenging yet important task for all researchers. Developing high quality small scale membranes is cost effective in research as unsuccessful units can be easily disregarded. Costs of rejecting unsuccessful large membranes is high, so the key challenge which must be addressed is to reliably prepare the high quality membranes on large surface areas integrated into process modules with high temperature sealing.
- Some research has dealt with trace contaminants such as sulfur, but real syngas streams contain a range of chemicals such as Hg, As, CN, etc. We suggest research in this area must incorporate the effects of trace contaminants on membranes. Catalysts in membrane reactors could be affected significantly by contaminants.

- More experimental studies of membrane reactor as well as computational work would be vital to the design of such membrane reactor systems.

Acknowledgments

GQL is grateful for the generous sponsorship for his sabbatical by the Carbon Mitigation Initiative of the Princeton Environmental Institute, Princeton University. Support from BP/Ford for the CMI program and from the Australian Research Council is also gratefully acknowledged.

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