Pd-based membranes for hydrogen separation: Review of alloying elements and their influence on membrane properties

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Abstract

Dense palladium membranes have increasing interest for ultra-pure hydrogen production compared to established technologies such as pressure swing adsorption and cryogenic distillation, allowing the separation in one step with no associated energy consumption. Among published reviews on Pd-based hydrogen separation membranes, to the best of our knowledge, there is no systematic revision of the alloying elements used in combination with palladium in these membranes. This paper presents a review of palladium alloy membranes for hydrogen purification, including permeability data and other relevant characteristics of the alloys. Further developments in this research field are expected to focus on the use of ternary alloys with enhanced physical and chemical properties, and the use of computational methods to enable a faster screening of promising alloys.

Keywords: Dense membranes, Metallic membranes, Hydrogen purification, Palladium alloys, Palladium permeability.

Contents

1. Introduction

The objective of this paper is to provide a systematic review of palladium-based alloys research and their use as hydrogen separation membranes, focusing on the different alloying elements studied so far and its effect on membrane properties. A brief introduction of Pd-based membrane properties and fabrication methods of supported membranes precedes the revision of the different alloys tested by researchers for hydrogen purification. An additional section reviews a novel feature: computational methods used to optimize membrane properties, a promising breakthrough that can speed up the discovery of novel alloys with enhanced properties.

1.1. Palladium-based membranes

Hydrogen is considered by many authors as the energy vector of the future, the so-called 'hydrogen economy' will provide low-emission transportation and power generation causing the hydrogen demand to rise up in the upcoming years [1,2]. The conversion of fossil fuels and biomass to H_2 requires a purification step in order to separate the hydrogen from reforming or gasification streams which contain gases such as CO, CO_2, N_2, H_2S, NH_3 and H_2O. Nowadays, hydrogen production and separation from gaseous streams is expensive due to high capital costs and the energy consumption of the associated processes such as compression, heat exchange, cryogenic distillation and pressure swing adsorption (PSA). Membranes for hydrogen purification are the most

promising candidates to replace traditional methods, allowing a notable reduction of the associated cost of the separation processes [3–5].

There are several types of membranes for hydrogen separation based on composition: metallic (dense and porous), inorganic (oxides, zeolites, glasses, and ceramics), carbon and polymeric [5,6]. Among them, dense metallic membranes are interesting because of their ability to produce high purity hydrogen using a single separation step, with low energy penalty, based on a solution-diffusion mechanism. Palladium, platinum, nickel and the metallic elements of groups III-V are capable of transporting dissociated hydrogen atoms through diffusion across a dense layer of metal [7], so, theoretically, a layer of these metals could transport hydrogen while blocking the path of other gases achieving infinite separation selectivity. However, due to the lack of physical porosity, the hydrogen flux is not as high as for the other kinds of membranes.

Membrane performance is generally described by its permeability, selectivity and thermal stability. Permeability measures the capacity of a membrane to process the permeate gases and denotes the flux through a membrane per unit of area and time at a given pressure gradient. Selectivity measures the ability of separating the desired component from the other components of the gas mixture and is usually determined by the permeation rate of pure hydrogen and other pure gas such as nitrogen and helium.

The diffusion of hydrogen through palladium is known since 1860s, when Deville and Troost observed that hydrogen permeated through several metals [8,9] and Graham

reported the absorption of hydrogen in heated palladium [10]. The interaction of hydrogen with palladium and its alloys has been widely investigated since then. More details on the historical evolution of the membranes can be checked out in Lewis book [11] and some recent reviews [12–15]. The mechanism of hydrogen permeation through palladium follows a solution-diffusion mechanism, consisting of dissociation of adsorbed H_2 onto the metal surface, diffusion of atomic H through bulk metal and associative desorption of the H_2 from the metal surface. Bulk diffusion can be considered as the rate controlling process for permeation through a metal membrane to simplify the calculations. An expression for hydrogen flux permeation through a dense membrane can be derived combining Fick and Sieverts' laws [14]:

$$J = \frac{\phi}{l}(P_{H,ret}^{0.5} - P_{H,perm}^{0.5})$$

Where J is the hydrogen flux through the membrane ($mol \cdot m^{-2} \cdot s^{-1}$), ϕ is the permeability of hydrogen ($mol \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1/2}$), l is the thickness of the metal layer (m), $P_{H,ret}$ and $P_{H,perm}$ are hydrogen partial pressure on the retentate and permeate, respectively. Hydrogen permeability is the product of diffusion and solubility, described by two well-known properties such as the solution and diffusion coefficients. Permeance has also been used to describe membrane permeation properties when the exact thickness of thin membranes is difficult to measure, or when the determination of the combined mass transfer resistances of the composite layers is desired. Permeance is calculated as the ratio of the hydrogen permeability to the membrane thickness. More detailed analysis

of the hydrogen permeation process, external mass transfer, surface adsorption and desorption, transitions to and from the bulk metal, and diffusion within the metal, can be checked elsewhere [16,17].

However, in some cases, the value of the exponent of the pressures was found not to be always equal to 0.5, so on a more general approach, this equation is usually written with both pressures raised by an exponent n. Through non-linear regression, the values of n, ϕ and the apparent activation energy, E (kJ/mol), can be obtained if flux data is taken at different temperatures and pressures. Exponent values equal to 0.5 indicate that bulk diffusion limits the mass transport of hydrogen through the membrane. For the early membrane works, this could be considered true in most of the cases but as the membrane becomes thinner, at some 'critical thickness' the solid-state diffusion will become rapid enough that other rate processes will begin to impact, and eventually limit, the permeation rate. For greater exponent values ($0.5 < n < 1$), hydrogen flux through the membrane is no longer inversely proportional to the membrane thickness. This effect have been attributed to different factors, including the increasing significance of surface effects that cause other types of hydrogen transport such as Knudsen diffusion, concentration dependence of the permeability, gaseous flow through defects, transport resistance of the substrate material, palladium surface contamination, flow of hydrogen through grain boundaries, thermal history, lattice dilatation and/or lattice defects [18]. When n=1, there is direct proportionality of hydrogen flux to the pressure

gradient. This indicates that the flux is being surface-reaction controlled rather than diffusion controlled.

Among other metals, palladium presents high catalytic activity to hydrogen molecule dissociation combined with high permeability towards diffusion of hydrogen atoms. Due to its favorable properties palladium and its alloys have been the most studied membranes for hydrogen separation. As an estimate value for state-of-the-art permeability of a pure palladium membrane, $1 \cdot 10^{-8}$ $mol \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-0.5}$ (at 400-500ºC) can be taken as reference [14]. Permeability data of pure palladium membranes with different fabrication methods have been collected elsewhere [18–20]. However, pure palladium presents a phase transition from α (interstitial hydrogen in solid solution) to β (palladium hydride) below 300ºC, resulting in a volume expansion about 10% which causes internal stress, crystalline structure distortion and an ultimate mechanical failure of the membrane. Both phases present fcc structure, with phase α having a maximum ratio of hydrogen (H/Pd) of 0.02, while phase β having a minimum ratio of 0.06 [11], and even though hydrogen occupies octahedral sites in both phases, lattice spacing of phases corresponding to a 3% linear size difference between the two phases [21]. Another major drawback of palladium membranes is the susceptibility to poisoning [22]. Sulfur poisoning, like produced by H_2S, causes corrosion and irreversible major reduction to the membrane permeability due to the formation of Pd_4S over the membrane surface [23–26]. CO is also found to be a poison for Pd membranes and it appears to have different effects depending on the temperature of the process. At low

temperatures CO is reported to show stronger effects, inhibiting the permeation of hydrogen due to a reduction of the hydrogen adsorption area [27,28]. At high temperatures two different effects were observed: CO adsorption and carbon deposition resulting from catalytic decomposition of CO on the Pd surface [29]. Steam [30], hydrocarbons [31,32], chlorine and mercury [33] are also reported to decrease hydrogen permeability of the palladium membranes.

In order to overcome hydrogen embrittlement and poisoning effects while trying to maximize hydrogen permeability, current research is focused on the development and optimization of Pd-based alloy membranes. To be used as hydrogen separation membranes, alloys must have high permeability, similar thermal expansion coefficient as the support metal (if used), adequate mechanical properties and the suppression of phase transition at the operating temperature. Palladium is able to form solid solutions with refractory and low melting point metals (10-30 wt%) and with rare earths (10-15 wt%) except for lanthanum and neodymium (2 wt%) [34]. When alloyed with structural isomorph metals (iron, nickel, copper, silver, gold…) palladium form continuous solid solutions in both binary and ternary systems. This fact widens the operating window and hence the potential applications of the membranes.

1.2. Chemical stability of Pd-based membranes

One of the most critical issues for practical applications in separation and reactors is the chemical stability of the membranes. The permeation of hydrogen through a palladium

membrane can result on a mechanical failure of the membrane due to embrittlement caused by phase change. Palladium alloys lower the critical temperature and pressure for the α/β phase transition by narrowing the α/β-Pd hydride miscibility gap in every palladium alloy except for rhodium [35]. Furthermore, the difference between the sizes of the α- and β-Pd lattice constants is closer in alloys so phase change distortion with hydrogen absorption-desorption cycles is reduced [14]. This effect is thought to be caused by the electron donating behavior of the alloying metals, being largely similar to the one of the hydrogen atom in palladium. Metal and hydrogen atoms would thus compete for the filling of electron holes in the 4d band of palladium.

Palladium and palladium alloy membranes have been used in membrane reactors for water-gas shift (WGS), steam reforming and hydrogenation/dehydrogenation reactions. The presence of other gases may affect membrane performance and lifetime. In this section, it is briefly described the poisoning mechanism of palladium membranes in the presence of H_2S and CO and how alloying metals can improve palladium poisoning resistance. However, there are other approaches to improve poisoning resistance such as modifying the metal membrane surface with a coating of another precious metal, or using nanostructured or amorphous alloy membranes. Research on these other approaches, as well as other poisoning species such as steam or coking effect, can be checked on the review on the chemical stability of Pd-based membranes written by Gao et al. [22].

The chemisorption of sulfur on the palladium surfaces has a strong impact on the surface properties of Pd membranes. The adsorbed sulfur atoms hinder the dissociation of H_2 on the membrane surface [36] and reduce the mobility of the hydrogen atoms [37]. The role of electronegative atoms such as S, Cl, and O as poisons for the adsorption of electron-acceptor molecules such as H_2 on Pd was studied by Lang et al. [38]. These poisoning atoms are thought to block "electronically" a region of several angstrom surrounding it. However, other researchers pointed out that the sulfur effect on hydrogen adsorption might be more complex. Wilke [39] found that the poisoning influence of sulfur is not only caused by a change of adsorption energy, it also might be caused by a decrease in the hydrogen adsorption rate in the presence of the sulfur adatoms.

The adsorption of CO on the surface Pd membranes have been explained as simultaneous adsorption or competition between CO and H_2. The adsorbed CO displaces the adsorbed hydrogen and further blocks hydrogen adsorption sites [40]. Inhibition effects of CO on hydrogen permeation through Pd-based membranes are reversible [29]; i.e., the hydrogen permeance of the membranes can be restored after CO is removed from the feed. This suggests that the coexisting CO is reversibly (competitively) adsorbed on the membrane surfaces. Therefore, temperature will play a fundamental role in preventing CO poisoning, reducing superficial CO membrane coverage with increasing temperature.

Adsorption of H_2S, CO or steam on the surface of an alloy is different from the adsorption on a pure metal. The alloying elements changes surface reactivity and the electronic structure of metal. Noordermeer et al. [40] studied the concentration of various Pd sites (triplet, doublet and singlet) for pure Pd and PdAg and PdCu alloys. From its geometric structure, a Pd-based alloy membrane decreases the poisoning effect of CO for the permeation of H_2 due to the reduction of triplet sites, which are the most favored positions for both CO and H_2. Moreover, the alloying elements changes the electronic band structure, reducing the Pd-CO bonding interactions for the case of PdCu. Similar reasoning also explains why some Pd-based alloy membrane can resist H_2S poisoning. Alfonso et al. [41] found out that sulfur forms stronger bonds and adsorbs preferentially in the three-fold coordination sites. Comparison of the binding energy on pure palladium and the alloy (PdAg and PdCu) surfaces showed no great difference. However, there is a trend to decrease of binding energy on the alloy surfaces. Opalka et al. [42] analyses revealed sulfur interaction with Pd-based alloys was predominantly controlled by electronic factors. They found a strong linear correlation of increasing adsorption strength (decreasing adsorption enthalpy) with increasing d-band center energy towards the Fermi level.

Surface segregation also have to be taken into account in the study of the poisoning effects. It is known that interaction with strongly adsorbing species such as sulphur can potentially induce surface segregation [41]. Consequently, the formation of any sulphide species may be accompanied by segregation of some of the alloy constituents to the

surface of the membrane. This effect can either lead to the irreversible chemical and structural modification of the surface, which can ultimately lead to membrane failure [42], or either can be beneficial to mitigate poisoning, as in the case of Pd–Au, where its sulphur tolerance is induced by a higher gold concentration on the surface caused by its preferential segregation [43].

1.3. Surface segregation in Pd-based alloys

A detailed study on structural and superficial composition is crucial to understand physicochemical properties of the membranes. The chemical properties of an alloy surface depend on the detailed surface composition and its related geometric and electronic structure, which is different from the surfaces of the parent metals and also differs substantially from the bulk alloy. In addition to understanding segregation at the clean alloy surface, it is important to understand how the components of the feeding gas stream affect the surface composition of the alloys. Surface restructuring in alloys during exposure to reactive environments, such as one where catalysis or corrosion occurs, can further modify the chemical composition of the surface, if one alloy component interacts more strongly with a gas phase species than the others, resulting in adsorbate-induced segregation [44]. Research on superficial segregation will play an important role in the analysis of the permeation properties of the membrane. Since it is usually not possible to predict the properties of alloy surfaces in a certain application by

knowing the bulk composition, the possible reactive molecules of the process environment must explicitly be considered.

Experimental studies of surface segregation have been done for most pure surface Pd-based alloys. It is well-known that silver surface segregates in PdAg alloys [45], and that also gold [46] and copper [47] surface segregate in Pd alloys. It has further been shown that Pd surface segregates when alloyed with Fe, Ni, Pt, Rh, and Ru [48]. However, in the presence of adsorbents, PdAg alloy presents a different behavior: while as in inert or vacuum atmosphere silver segregates to the surface of the alloy, reversed surface segregation of Pd in PdAg alloys is reported in the presence of hydrogen and carbon monoxide, due to the chemical interaction between the adsorbate and surface atomic sites [49,50]. After high temperature operation studies, using XPS and AES, major segregation effects were observed, reporting an increase of Ag/Pd ratio up to 32% [51]. Segregation effects were also reported using XPS depending on the annealing temperature [52]. Surface segregation of PdCu alloys in the presence of hydrogen have also been studied to some extent. Miller et al. [53] studied the influence of the annealing temperature and fabrication method of PdCu membranes on the surface region. Two different zones were spotted: the near-surface region, where copper remain below the concentration of the bulk, and the top layer region, which is copper rich relative to the bulk. Their results showed that in spite of having nearly identical surface region and top layer compositions, absorption of hydrogen is affected and is thought to be caused by the local arrangement of atoms on the top surface caused by

annealing temperatures. Computational studies on PdCu alloy also predict a Cu-rich/Cu-depleted top layer/second layer [54]. The behavior of the surface of other Pd-based alloys in the presence of hydrogen, such as PdAu [55,56] or PdPt [57], is also available in the literature.

Due to the permeation process, hydrogen is not only in contact with the surface of the alloy but also with the bulk; as a consequence, homogeneous fcc-Pd alloys have been found to undergo lattice rearrangements, such as phase separation, in the presence of dissolved hydrogen. Flanagan and Park [58] reviewed the phenomenon of hydrogen-induced lattice migration (HILM). They reported that some Pd-based alloys form a ternary equilibrium which may be accompanied by phase separation, resulting in two phases with different metal and hydrogen compositions. This effect was reported to occur on PdRh, PdPt and PdNi alloys while PdAg alloys are relatively unaffected.

1.4. The role of the support on Pd-based membranes

Palladium-based membranes can be classified depending on their structure or fabrication method. There are two types of membranes according to their structures: self-supported membranes or membranes deposited onto porous supports. Yun and Oyama made an excellent review on the influence of the support and the fabrication methods on the membranes [59] in which several correlations for structure and function are presented. Another review of special relevance is the revision of the supported Pd-based membranes history and evolution on the 1990s decade written by Uemiya [20].

Unsupported membranes were used since the discovery of the hydrogen permeation through palladium until the late 1980s. These membranes were made by metallurgical processes and used in stand-alone form, without any auxiliary component sustaining the top metal layer, allowing great control of the composition of the membrane and a cheap manufacture. In fact, self-supported membranes have been commercialized and are installed in some hydrogen purifiers from SAES Pure Gas. However, the low flux of hydrogen due to high film thickness and the excessive amount of metals used are major disadvantages. Although some studies use unsupported membranes nowadays, the use of these membranes among researchers has fallen into disuse.

Palladium film thickness is one of the most important membrane characteristics affecting hydrogen permeability. Considering the atom diffusion through the palladium as rate determining step, by using Sievert's Law it can be derived that hydrogen permeability and film thickness have inverse proportionality relationship. Since a thickness of 20µm (with a tubular geometry) is required for mechanical stability of an unsupported membrane [14], state-of-the-art research is focused on supported membranes. Porous supports have allowed membranes to reduce film thickness below 1µm, obtaining great increase of membrane permeability compared to unsupported membranes. Supports provide structural integrity while not impeding hydrogen permeation due to their porous structure. Vycor glass, ceramic and metallic materials have been used as supports. However, supported membranes also have some drawbacks such as the permeation resistance of the substrate itself, poor adhesion of

the films [60] and element diffusion from the support to the metallic films at high temperatures [61–63], that can cause permeability losses and ultimately membrane failure.

Vycor glass is a borosilicate glass with a regular porous network and small size pores (4-300 nm) and was the first support used in palladium electroless plating by Uemiya et al. [64,65]. Nowadays Vycor glass has fallen into disuse due to its low thermal resistance. Sinterization at 550ºC was reported causing the collapse of the porous structure, lowering to 450ºC in hydrothermal conditions [66].

Ceramic supports are widely used as membrane supports due to their high permeability and chemical and thermal resistance. Most of the manufactured ceramic supports present asymmetric structures, which are made of several layers of particles with different sizes, opening the possibility to tune the porosity in the layer in contact with the metallic film. Asymmetric membranes are manufactured by depositing layers by dip-coating, slip-casting or sol-gel on high-porosity ceramic support [67]. The most common compounds for membrane supports are alumina, silica or titania. However ceramic membranes are difficult to assemble, seal, and handle to make a module. Moreover, fragility, worse resistance to thermal shock and poor film adhesion [68] are other major drawbacks.

The vast majority of metal supports are made of porous stainless steel (PSS). Metallic supports are manufactured by compression and/or sintering of small metallic particles.

PSS properties include mechanical and corrosion resistance, thermal coefficient similar to Pd and its alloys, cheap manufacture and easy attachment to the process by welding. Other metallic materials have been used as membrane supports such as Ni [69,70] or TiAl [71,72]. The major disadvantage of metallic support is the lack of control and distribution of porosity and smoothness of the surface. Size and distribution of the pores on the support plays a fundamental role in the deposited film quality, preventing defect formation and reducing the thickness of the metallic layers [73]. Smoothness will also be crucial in the control of the film thickness, Mardilovich and coworkers studied platinum deposition and film formation onto porous supports depending on the smoothness of the support [73], concluding that rough surfaces will need thicker films to achieve a continuous metallic layer. However, film adhesion is favored in rough surfaces and large pores [60], so a compromise between a proper adhesion and an adequate film thickness must be achieved.

In order to tune the pore size of the metallic layers, deposition of intermediate layers has been used to achieve the optimum pore size and uniform deposition. It is reported that the thickness of the Pd layer must be approximately three times the dimension of the largest pores in the support [73]. The application of an intermediate layer can also be used to prevent intermetallic diffusion between the support and the Pd alloy, in which case are referred as diffusion barriers. Ceramic materials, such as SiO_2 [74,75], Al_2O_3 [76], ZrO_2 [77] or YSZ [78], are among the most used intermetallic layers. Other

types of intermediate layers such as Fe_2O_3 [76] NaA zeolite [79], TiN [80] or oxides from support oxidation [81] have also been used.

1.5. Fabrication methods

Most common methods for preparing supported palladium membranes are physical vapor deposition (PVD) by the use of the magnetron sputtering technique and electroless plating. Chemical vapor deposition (CVD) has also been used to some extent [82–85], but the resulting microstructure changed the traditional solution-diffusion mechanism of dense metals to diffusion through the surface of the metal grains [86], resulting in low selectivity values. Palladium based membranes can also be manufactured using other methods such as electrodeposition [87–89], spray pyrolysis [90], wet-impregnation [91] and pulsed laser deposition [92], but the use of these techniques is uncommon with very few examples present in the literature.

PVD produces deposition of a solid material onto a support by condensation of the vaporized form of the desired film material with no chemical reactions involved in the process. Specifically, magnetron sputtering is a plasma coating process in which desired material is ejected due to bombardment of ions. This technique is able to produce nanostructured and very thin films with great control of alloy composition with minimum presence of impurities [82,93]. Some problems associated to this method have been reported so far: grain growth and phase transitions at 200 °C [94] due to small grain sizes, problems with film adhesion to the support [95,96], great dependence

of substrate condition to fabricate defect-free films [97] and expensive and complicated processes to produce membranes with no defects [98,99].

Electroless plating (ELP) is a chemical method for metal plating based on autocatalytic thermal reduction of Pd complexes facilitated by a simultaneous oxidation of a reducing agent in aqueous solution. The film grows on previously seeded Pd nuclei on the surface by activation and sensitization processes. ELP recipes are only available for a limited number of elements with high-reduction activity, although it might be considered as a disadvantage, some of the most used Pd-alloying (Ag, Cu, Au, Ru, Pt and Rh) metals can be deposited using this technique. ELP is a cheap technique, easy to scale up and have the ability of easy film deposition in non-planar supports. However, ELP has worse film control thickness and may result in impurity presence on the alloy. Over the years, significant advances have been achieved in electroless deposition onto porous supports, such as new activation methods without tin containing sensitizers, which used to be a source of impurities [100–102], ambient temperature ELP [103], correlations between quality of the film and the grain size versus the operation conditions [104], combination of conventional plating with osmosis, resulting in a densification of the metal layer and reduction of defects [105,106], palladium recycling for the preparation of new membranes [107] or the 'pore-plating method' which consists on feeding both plating solution and reducing agent from opposite sides of support [108].

Depending on the film fabrication method and its operation conditions, films can have different microstructures. The microstructure of the metallic film will play a fundamental role in hydrogen permeability, selectivity and thermal stability. In fact, there are discrepancies in permeability values that cannot be explained by the differences in membrane thickness and composition that might be caused by differences in the microstructure. The effects of the microstructure on hydrogen permeation might be important but have not been systematically studied yet [109]. Some authors reported permeability enhancements after annealing at high temperatures, showing that increasing the grain size had a beneficial effect on hydrogen permeation in ELP [104] and sputtered [109] membranes, attributed to the increase of diffusivity of the metal layer [110]. For nanocrystalline microstructures (below 40 nm), hydrogen diffusion through grain boundaries instead of lattice diffusion is reported to occur in metallic membranes [111], coexisting with lattice diffusion up to 100 nm of grain size. Grain boundary diffusion has been reported in electrodeposited PdFe [112,113] and PdNi [114,115] membranes. The excess of free volume in grain boundaries results in enhanced solubilities, allowing a fast diffusion of hydrogen and change of the rate limiting step of the process. However, the intercrystalline spaces also allow the diffusion of undesired gases, affecting membrane selectivity. Thermal stability above 450ºC for palladium dense membranes prepared by ELP has also been questioned depending on microstructure. Guazzone and Ma [116] reported selectivity losses and

formation of pinholes attributed to the incoherent sintering of Pd nano-crystallites due to palladium self-diffusion.

On the enormous effort of maximizing hydrogen permeability, researchers have also explored the use of activation methods on the membranes prior to their use. A number of studies reported high permeability improvement after exposition to air or other oxidative atmospheres at high temperatures, after-treatment permeability is reported to be increased in some studies even to the double of its original value. Positive results have been achieved using pure palladium membranes [28], in which enhanced permeability and CO resistance is achieved. Studies have also been performed in Pd-based alloys such as PdAg [117–119] or PdCu [120], in which the same effect was observed. Increased surface roughness, probably due to the formation and subsequent reduction of palladium oxide, resulting in increased number of active sites for hydrogen dissociation has been observed after treatments together with the removal of contaminating species present in the membrane surface [118]. However, the exposition might also cause an irreversible rearrangement of PdCu in the surface creating micropores [120]. Chemical cleaning has also proved to be an efficient activation method, and thus permeability increases by a factor of 2 have been reported on PdRu membranes [121].

2. Binary Pd-based alloy membranes

In this paper, discussion on binary alloys is divided into different sections: Group IB metals, i.e. silver, copper and gold, which are the most studied alloying metals, are discussed in three separate sections. Platinum-group and rare earth metal alloys have also been collected in independent sections. The last section will include the rest of the alloys that have been collected. Each section contains a table in which alloy composition, support, thickness, preparation method, pure hydrogen permeability, temperature and the ratio between permeability of the alloy and pure Pd are collected. Pure Pd permeability to calculate the ratio is only taken if the membrane is fabricated by the same group and using the same fabrication method and operation conditions.

2.1. PdAg alloys

Silver addition to palladium gives rise to a stable alloy with fcc structure, which reduces the temperature for metallic hydride formation which causes hydrogen embrittlement and affecting membrane permeability. The first patent using PdAg membranes for hydrogen separation was registered in 1956 [122]. PdAg alloy have been the most studied Pd-based membranes over the years and currently can be found in small commercial applications. Early studies on supported membranes found that optimum permeability of this alloy is achieved with 23 wt% alloy [123], as shown in Fig. 1. At silver contents over 20% in the alloy, mechanical stress of membrane is considerably suppressed due to smaller difference of lattice parameter between α and β phases

[124]. However, recent studies shown nitrogen leakage in thin films (2-4 μm thick) due to mechanical stress at temperatures below 100ºC [125].

Electroless plating of PdAg is a well-established technique and it is widely used for PdAg membrane production. PdAg can be deposited using both simultaneous ELP [126–129] or sequential ELP [130–133] followed by annealing. Sequential ELP consists on the deposition of alternative layers of Pd and Ag followed by a thermal treatment to force metallic interdiffusion of the metals. Good control of alloy homogeneity, that directly affects bulk permeability, is hard to achieve using sequential deposition and it depends on the thickness and composition of the layers and conditions of the thermal treatment [126]. Annealing after sequential deposition must be carefully performed since it could produce element diffusion from the support to the alloy, causing additional permeability losses [134]. Simultaneous deposition annealing can be carried out at low temperature because the metal particles are homogeneously dispersed onto the support [126,127]. Hence, simultaneous ELP also allows better control of the homogeneity and reduces process temperature. However simultaneous ELP is extremely sensitive to process variables, such as deposition time, temperature and plating solution [135,136].

Magnetron sputtering was also extensively used to manufacture thin PdAg films onto porous supports, however early studies showed poor values of hydrogen permselectivity and pinholes in the membrane [82,96,97]. Alternative methods were proposed from the direct deposition onto the porous support. Mejdell et al. developed

the so-called two-step process: In this method, the thin defect-free Pd-alloy film is sputtered onto a non-porous silicon wafer, and afterwards, the film is removed from the wafer and can either be used self-supported or integrated with a porous support [137]. Gielens et al. proposed an alternative method to produce pinhole-free PdAg sputtered alloys using microsystem technology, in which the PdAg film is deposited on a non-porous silicon nitride layer and porosity is created afterwards by etching to create a clear passage for hydrogen [98].

Despite the enhanced permeation properties of the alloy, as shown in Table 1, PdAg is sensitive to sulfur poisoning. Sulfurous compounds (Pd_4S and $Ag_5Pd_{10}S_5$) formation on the alloy surface were reported like in pure Pd membranes [138]. The strong interaction between H_2S and Pd can also cause Pd segregation to the membrane surface [49] modifying bulk and surface properties of the membrane. However, unlike pure Pd membranes, H_2S seems to not produce selectivity losses or defect formation [139]. Chlorine has also been reported as a poison with more harmful effects than sulfur [140]. PdAg membranes have been studied extensively for the separation of hydrogen from the main components of synthesis gas, with good results for non-sour syngas, permeability and durability. Data of PdAg alloys performing separation of hydrogen from the main components of syngas can be checked elsewhere [141–144].

2.2. PdCu alloys

Palladium-copper membranes have been widely studied due to the suppression of hydrogen embrittlement at low temperatures, reduction of membrane cost due to the low price of copper and its most important property, the great resistance to sulfur poisoning compared to pure Pd and PdAg. McKinley discovered the beneficial properties of the alloy and patented it more than 40 years ago [145]. Studies reported permeability losses even with small additions of copper, and, as copper concentration of the alloy increases the permeability losses also increase. However, maximum permeability appears with $Pd_{60}Cu_{40}$ alloy, due to the formation of a bcc crystal lattice instead of fcc [146]. To corroborate that hypothesis, hydrogen permeability of PdCu alloys have been tested at different temperatures and pressures and it have been attributed only to the phase change [147]. Hydrogen diffusion in bcc phase is two orders of magnitude higher than fcc [148], while solubility in bcc is lowered [149], but overall, the hydrogen permeability is higher in bcc-PdCu [150,151]. Recently, it was found that temperature cycling of bcc-PdCu over the miscibility gap, results in compositional segregation and heterogeneity of the alloy [152] and permeation hysteresis [151]. Crystallographic structure of the alloy depending on the element concentration was investigated in a number of research publications [153–157]. One of these phase diagrams is presented in Fig. 2 (without taking into account the effect of the dissolved hydrogen) together with permeability values at several concentrations. Permeability values of selected works have been also collected in Table 2.

Contrary to the permeation behavior, poisoning resistance has been proven to be better in fcc than bcc phase [24,158]. This effect is believed to occur because of electronic factors [42]. For example, Mundschau reported a 20% reduction of the permeability of fcc-PdCu exposed to 20 ppm of H_2S and a loss of 90% in bcc phase [138]. Morreale et al. reported a 10% permeability loss in fcc with 1000 ppm of H_2S while bcc losses affect 99% of the permeability below 400 °C [159]. A recent study proved that Pd and PdCu membrane failure by sulfur poisoning depends on H_2S concentration rather than time of exposure, with maximum admitted concentrations of 100 and 300 ppm respectively [160]. Long term stability tests with fcc alloys up to 20 wt% of Cu showed surface sulfides at 500°C blocking adsorption sites and reducing hydrogen permeability to 80% of its initial value [61]. Studies with WGS mixtures showed reverse WGS reaction 10 times higher than in pure Pd membranes, since Cu-based alloys are used as WGS and CO oxidation catalysts. Moreover, the exposure to CO and CO_2 caused Pd segregation and defects on the membranes, resulting in a decrease of membrane selectivity [161].

Supported palladium-copper membranes can be prepared using sequential electroless deposition followed by annealing [162–164], showing excellent selectivity and durability [165]. Annealing and segregation during preparation were studied by Golbach et al. and reported PdCu alloys with excellent homogeneity control [166]. Pomerantz and Ma, recently developed a new method to manufacture a dense Pd membrane with PdCu on the surface of the membrane by the deposition of sub-micron layers of Cu by electroless

plating and Pd by the galvanic displacement of Cu on top of an already dense Pd membrane [167].

2.3. PdAu alloys

Right after silver and copper alloys with palladium, the third most studied alloying material is gold. PdAu has enhanced poisoning resistance compared to pure palladium and it was patented by McKinley in 1967 as a material for hydrogen purification membranes [168]. In this patent, it was reported that membranes with 40 wt% of gold decreased greatly the inhibition of hydrogen permeability in gaseous streams containing H_2S and membranes with 1-20 wt% gold improved hydrogen permeability up to 30%. Further studies on hydrogen permeability on PdAu alloys claim that 11 at% content of gold is the optimum gold addition to maximize permeability [169] at high temperatures, agreeing with theoretical predicted results [170]. Hydrogen permeability of PdAu alloys with contents up to 20 at%, yielded improved permeability values compared to pure Pd membranes [169,171], but for higher contents of gold on the alloy it starts to rapidly decrease, as seen in Fig. 3. Chen and Ma studied the resistance of a low gold content alloy ($Pd_{92}Au_8$) to H_2S at high temperatures and observed no bulk sulfide formation with full hydrogen permeation recovery after 55 ppm H_2S exposition, showing that permeability decline on PdAu membranes was only caused by dissociative adsorption of H_2S [172]. However, further studies at lower temperatures detected small permanent reductions of the hydrogen permeability in long run tests with H_2S [173].

Although in the previous articles, membranes were fabricated using magnetron sputtering and metallurgical processes, there are also studies using electroless plating. The classical electroless plating bath for gold contains cyanide [174], but recently a non-basic cyanide-free bath has been developed [175,176]. Shi et al. used this method to manufacture PdAu membranes using sequential ELP, reporting thin membranes (3-5 μm) with no defects and enhanced permeability up to 500 °C [177]. However, the annealing process remains a challenge, and obtaining a completely homogenous alloy is much more difficult than in PdCu alloys [177,178]. It is also reported that the microstructure of the PdAu alloy created by different fabrication techniques, has great effects on hydrogen permeability, as it is shown in Table 3.

Gade et al. also reported the influence of the alloy composition and membrane fabrication on the resistance towards sulfur poisoning using sour syngas in membranes with gold content up to 20 wt% [179] and found out that as gold content increased, hydrogen permeation inhibition decreased. In that work, they also reported that magnetron sputtered membranes are more easily poisoned than metallurgically prepared ones, observing severe metal losses in sputtered alloys due to corrosion causing early failure of the membranes. Other studies attributed this effect to the surface roughness of the membranes, since mechanized membranes are smoother, they are supposed to absorb less H_2S in their surface [160]. 20 wt% gold content was found to be the best composition for gas mixtures, with sulfur-free WGS showing no permeability losses and a 60% inhibition in the case of WGS with 20 pmm of H_2S. Long

run tests in coal derived syngas showed the exceptional robustness of the PdAu membranes with syngas with actual industrial parameters [180].

2.4. Alloys with platinum-group metals

Hydrogen purification membranes using PdRu alloy have also been patented in the 1960s [181]. Small additions of ruthenium resulted in an improvement of the mechanical properties of palladium [182–184] and thermal stability of the membrane [185], reducing the growth of defects resulting in inert gas leaks. Hydrogen permeability of the alloy with 4.5-10 wt% ruthenium (Table 4) is similar to the permeability of pure Pd [184], with an optimum composition in terms of hydrogen permeability around 5 wt% of ruthenium, contradicting the initial values reported by Knapton [35]. Early PdRu membranes were prepared by metallurgical methods and were known to have excellent properties for low temperature permeation [34]. However, nowadays PdRu is prepared by electroless plating: ELP co-deposition showed rather good results [184–186], but sequential deposition is reported to not form homogeneous phases even with long annealing times [187]. Alloy strength is reported to be increased up to 80% in comparison with pure Pd membranes [184], with values similar to CVD deposited films, in which materials presents small grain sizes. In the former Soviet Union, PdRu alloys have been widely studied over the years for a number of applications, such as membrane reactors [188,189], and in the hydrogenation of organic compounds [190–192] or CO_2 [193]. In a recent study, the alloy has been also proposed to be used in

steam reforming processes [194] in membrane reactors. There is another study worth mentioning even though it does not use a PdRu alloy but a Pd/Ru composite, in which a nanometric scale-sized film of Ru is grown on top of a palladium film, achieving a surprising enhancement of hydrogen permeability of 1.4 times the permeability of pure palladium [195].

Platinum as alloying element has also been investigated due to pure platinum resistance to sulfur poisoning compared to palladium [26,196]. However, due to the low permeability values of platinum it cannot be used as pure metal. PdPt electroless deposition is also a well-known method capable of producing thin films. Pt additions between 5-26 wt%, are reported to enhance palladium selectivity, while reducing the permeability [197]. Although permeability values shown in Table 4 do not seem promising, platinum produces great enhancement of mechanical properties [198] and thermal stability of the film, allowing stable permeation up to 650 °C and reducing the leak formation in long term operations [185]. Also, the alloy has excellent resistance to poisoning. It has been reported that Pd_4Pt alloy membranes only suffered an inhibition of 50% of the original flux upon exposure to 1000 ppm of H_2S and allowed a full recovery of the original flux after exposition [199]. Upon exposure to WGS mixtures, PdPt also showed a reduction of the inhibition due to WGS in comparison to pure Pd membranes, showing higher hydrogen fluxes even with its reduced permeability in pure hydrogen [197].

Rhodium has also been studied as palladium alloying element, but to a lesser extent than ruthenium and platinum, even though PdRh presents interesting properties: the alloy can be deposited using electroless plating, mechanical properties of PdRh are reported to be similar to PdPt alloys [198], and permeability on pure hydrogen is enhanced compared to pure Pd [200].

2.5. Alloys with rare earths

During the 70s I.R. Harris and his colleagues conducted extensive research, both structural and metallurgical [201], on palladium alloys with rare earth metals such as yttrium, cerium and gadolinium as well as their use as hydrogen permeation membranes [202]. Due to the larger size difference between palladium and rare earths a solid solution hardening and lattice expansion was predicted for these alloys. 5.75% Ce, 8% Gd and 8% Y (at%) were found to be optimum concentration of these elements in palladium alloys. Results, collected in Table 5, show great enhancements of hydrogen permeability using these alloys in comparison with PdAg due to the substantially greater solubility gradients [202].

Cerium has strong dependence on temperature and pressure in the hydrogen permeation process. As it can be seen in Fig. 4, the best performance is observed for the addition of yttrium, while cerium shows enhanced permeability compared to PdAg at temperatures over 350ºC and it was also found that lowering the differential pressure resulted in additional permeability losses [203], with values similar to PdAg. These

results are in disagreement with Knapton data of PdCe (6 at%) [35], who reported significant permeability losses.

Studies on mechanical properties of yttrium showed that there are not dimensional changes upon hydrogenation and similar thermal expansion and increased strength compared to PdAg alloys [204]. However, yttrium revealed severe corrosion problems after oxidative activation steps. In the alloy surface it was detected preferential oxidation of yttrium to produce Y_2O_3 which is not strongly bonded to the surface of the membrane and leaves behind a layer of enriched PdY, caused by the depletion of yttrium from the surface [205]. Poisoning effects of CO [206] and hydrocarbons [207] in PdY membranes have also been reported.

Based on Harris good permeability results, Y. Sakamoto also studied binary alloys of yttrium and gadolinium as basecase for the development of novel ternary alloys [208]. In these studies, unsupported membranes were also used and in both cases there is a great improvement of the permeability, similar to the data reported in Harris articles. As it can be seen in Table 5, in this study, gadolinium has a better effect on hydrogen permeability than yttrium.

With the objective of finding new elements to maximize hydrogen permeability, Kang et al. used computational methods to identify new alloying elements for Pd-based membranes with composition of $Pd_{96}M_4$. These simulations shows that the most favored alloying elements in order to increase permeability are thulium and europium

[209]. Simulation results were checked experimentally with a sputtered PdTm membrane and very positive results were achieved. Permeability of the membrane increased 50% in comparison with PdAg and doubled the permeability value of pure palladium. However, the rarity and high price of thulium plus the severe hydrogen embrittlement detected in permeation test, make this binary alloy unattractive as a hydrogen separation membrane.

2.6. Other binary alloys

Pure group VB metals (vanadium, niobium and tantalum) with bcc structures have excellent hydrogen permeability, as it can be seen in Fig. 5, depicting permeability data collected by Steward [7]. However, these bcc metals present reduced catalytic activity for hydrogen dissociation and reassociation due to the formation of very stable passive oxides on the surface [210] and significant permeability reduction with increasing temperature.

One might think that VB metals might be appropriate candidates as palladium alloying elements, but these alloys do not present good properties as hydrogen separation membranes. Research efforts using VB metals in combination with palladium focused on using bcc metals as dense metallic supports due to their good permeation properties with a thin layer of palladium on both sides for catalytic dissociation and reassociation of hydrogen molecules. These composite metallic membranes need intermetallic layers

to prevent metallic interdiffusion, since the formation of Pd-VB alloys are reported to cause severe hydrogen embrittlement and permeability losses [210–212].

The limited available data of hydrogen permeabilities with Pd-VB alloys is collected in Table 6. PdNb and PdTa deposited using magnetron sputtering [213] and CVD PdNb [214] show lower permeability compared to pure palladium. Admixture of relatively small amounts of VB metals to palladium leads to alloys with quite different behavior from PdAg or PdCu. Since VB metals possess higher hydrogen solubility than palladium at membrane operation pressures and temperatures, comparing the alloy with a standard PdAg alloy, VB metals are thought to take the place of palladium, while palladium takes the place of silver. Thus an addition of vanadium or niobium to palladium produces hydrogen traps causing a prompt and clear decrease of the diffusion coefficient [215,216]. Solubility decline of these alloys compared to pure palladium has also been reported for PdV [217] and PdNb [218]. Since permeability is a function of diffusivity and solubility, these results are in agreement with the reported permeability losses and confirm the poor performance of Pd-VB alloys as hydrogen purification membranes. Chemical reactivity of the surface of vanadium [219] and niobium [220] alloys will also cause sensitization of the surface of metal films towards poisoning.

Due to the good results in permeability achieved with the addition of rare earths caused by lattice expansion, Sakamoto at al. studied the effects on the permeability of palladium binary alloys with indium, tin and lead [221]. Those white metals are known

to bring larger lattice expansion than PdAg, but the results were not correlated with permeability, as it can be seen in Table 6. Compared to pure Pd, permeability of PdIn is not affected at all, while PdPb permeability is enhanced and PdSn suffers an important reduction.

Nickel has been reported to be an interesting alloying metal for palladium, resulting in alloys with increased hardness and ductility and less susceptible to embrittlement [222]. PdNi membranes were deposited using electrodeposition [114,115], CVD [214] and ELP [223] techniques. Electrodeposited membranes produced very thin films with low selectivity, acceptable permeability and a hydrogen partial pressure exponent close to 1 [114] thought to be caused by diffusion via grain surface instead bulk lattice [115]. In fact, at operation temperatures of 600ºC, selectivity grows to values >4000 from values below 1000. This could be caused by sintering of the fine grains. Both CVD and ELP PdNi have produced thin films with no defects and lower permeabilities with even less content of Ni, as it can be seen in Table 6, so this alloy does not seem to be a good candidate for hydrogen membranes in terms of permeability.

Internal oxidation (IO) of PdM alloys, where M is a metal more readily oxidizable than Pd, results in a matrix of pure Pd with nano-sized oxide precipitates. IO is found to be a convenient method to enhance hydrogen adsorption rates of palladium [224]. There is a study on PdAl as membrane material [225] in which 0.02-0.1 at% Al was added to pure palladium, due to the enhanced resistance to CO poisoning showed by internally

oxidized PdAl alloys [226]. Results show a reduction of pure hydrogen permeability but a great resistance to CO poisoning. Hydrogen flux of IO-PdAl is very similar to the unoxidized alloy, so the oxidation treatment is believed to affect superficial properties of the alloy, favoring hydrogen adsorption instead of CO on the surface of the membrane. The addition of 0.02-0.15 at% of Fe to palladium was investigated by the same authors that studied IO-PdAl. Increasing the Fe content of the alloy causes drastic reductions of the permeability as shown in [227]. PdFe internally oxidized alloys have greater hydrogen fluxes than unoxidized PdFe and are less likely to leak due to the formation of cracks or pinholes than PdAl alloys.

Iron has also been used to stabilize the grain growth in nanostructured films produced by pulsed electrodeposition where Fe is expected to eliminate palladium phase transition and stabilize grain growth due to Fe_2O_3 precipitation at grain boundaries via solute drag [112,113]. Results show that increasing the Fe content resulted in enhanced stability of the grain structure until 20 at% of Fe in the alloy. Above that value, the alloy was stable against grain growth at 400ºC [112]. Nanostructured PdFe membranes showed acceptable hydrogen fluxes and enhanced resistance to H_2S and CO. Membranes with contents of 5-10% Fe, showed severe grain growth at 400ºC, resulting in a drastic decrease of hydrogen flux and selectivity losses due to apparition of pinholes [113], making alloys with contents below 20 at% Fe unsuitable for high temperature processes. From the data collected in Table 6, it is especially surprising the enormous reduction of the permeability reported in the IO-PdFe in comparison with

electrodeposited PdFe. However, the selectivity of these layers is really low, with values around 30:1 (H_2/He) due to their microstructure. Moreover, suitable compositions for high temperature operation, varying from 20% and up to 28 at%, which is the maximum content of iron allowing hydrogen diffusion [113], have very low hydrogen permeability.

Amorphous PdSi alloys have also been studied as possible candidates as membranes for palladium membrane reactors [228,229]. As Itoh et al. pointed out, amorphous alloys are thought to have good catalytic activity for processes such as methanation and hydrogenation [229] and until their research only electrochemical studies on diffusivity and solubility below 100°C were made. Although hydrogenation activity was found for this alloy, the hydrogen permeability is in the order of 10^{-10} $mol \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-0.5}$, so it does not seem to be a proper candidate to be used as hydrogen permeation membrane material. Si is known to form amorphous alloys with interstitial character which does not obey Sieverts' law [230]. As germanium also forms amorphous alloys with palladium in the same way as Si, similar results were reported for PdGe alloys [231]. While substitutional alloys may increase permeability, interstitial alloys often decrease hydrogen permeability by blocking hydrogen diffusion paths or acting as traps. Boron is another example of this behavior [232], causing permeability losses by distortion of hydrogen pathways by the atom in an interstitial position.

3. Ternary Pd-based alloy membranes

Similarly to binary Pd-based membranes, ternary membranes have been subdivided in three groups: PdAg-based, PdCu-based and rest of the alloys. Each subsection will also include a table with the data collected for the binary alloys plus another ratio between the hydrogen permeability of the ternary alloy and the binary alloy (i.e. the alloy of Pd with the second compound on the ternary alloy formula).

3.1. PdAg-based ternary alloys

PdAg alloy poisoning resistance is reported to be bad, so the development of Pd-Ag based ternary alloys aims to use PdAg excellent permeation properties and the poisoning tolerance of a third element. T.A. Peters et al. have modeled sulfur resistance of PdAg-X alloys [233] and performed a systematic study of $PdAg_{20}X_5$ (with X = Au, Mo, Cu and Y) analyzing the poisoning resistance of the alloys in the presence of H_2S [234]. Hydrogen permeability suffers a great reduction with all the metals except Y compared to PdAg as it can be seen in Table 7. Sulfur poisoning resistance was tested with 20 ppm of H_2S in H_2. Ternary alloys containing Y and Mo, are found to be inadequate for H_2S environments since they show important large segregation and oxidation effects and sulfur incorporation to the alloy. PdAgAu showed the highest effective hydrogen permeance in the presence of H_2S, improving twice the value recorded for a PdAg membrane. PdAgCu did not show significant improvement of the permeability in the presence of H_2S, but allowed an important recovery of the original flux after the exposure. In a later study, PdAg-based alloys segregation effects were modeled using

DFT in order to evaluate the effect of the atomic segregation of the third alloying element on the sulfur stability on the alloy surface [233].

Gold addition to PdAg alloy has also been studied by other researches, with the objective of improving PdAg H_2S resistance. In those works, PdAgAu membranes have been fabricated using electroless plating [235–237]. In Table 7 it is shown that hydrogen permeability of this alloy is approximately the same as the values that can be obtained using pure palladium. Sulfur poisoning resistance is reported to be excellent, with no sulfur formation on the surface of the alloy, a flux inhibition reduction by a half compared to pure Pd and 80% of flux recovery after the exposure [235,236]. Other authors reported a flux inhibition of 29% in sour (20 ppm H_2S) WGS gas mixture and a 97% flux recovery in WGS gas after removing H_2S [237], and found that temperature plays a major role in reducing the effect of poisoning. However, gold and silver segregation to the exposed alloy surfaces [235,237] was detected.

Ruthenium addition to PdAg led to great enhancement of hydrogen permeability with good selectivity. Pd-Ag-Ru prepared by simultaneous electroless plating [238] exhibits a hydrogen permeability 3-4 times higher than pure Pd and more than 2 times compared to binary PdAg.

3.2. PdCu-based ternary alloys

PdCu alloys with fcc structure have a great chemical resistance and great mechanical properties but low hydrogen permeability compared to pure Pd. In order to improve the

permeability while maintaining the good properties of PdCu, many researchers have investigated an addition of a third element to the alloy. Potential properties of PdCu-M alloys were modeled using first principle calculations [239], predicting that the addition of Au, Ag, Ru or Rh would improve membrane permeability while maintaining the poisoning resistance [240]. Alternatively, other authors tried to identify bcc-PdCu ternary alloys with enough chemical and physical stability while maintaining the high permeability of the bcc structure [241]. Taking these studies as reference, Peters et al. realized a systematic study of the effects on hydrogen permeability of the addition of another metal to the PdCu alloy [213]. The permeability of PdCu-TM (with TM = Ru, Mo, Ta, Au, Ag and Y) fabricated by magnetron sputtering have been studied and compared with their corresponding PdCu and PdM binary alloys. All the membranes tested with 1 at% of TM, always resulted in increased permeability compared to binary PdCu. The best results were obtained with tantalum (1%), yttrium (1%) and silver (14%), but the maximum permeability obtained is only around 50% of pure palladium permeability, as shown in Table 8.

In a later work, continuing the ab initio calculations, it was predicted that addition of small amounts of silver would improve hydrogen diffusivity and solubility, hence improving permeability. Moreover, using density functional theory (DFT), the permeability of a wide range of concentrations of PdCuAg with fcc structure was predicted and depicted in ternary diagrams [242]. It was concluded that the enhancement of the permeability was caused mainly by increase of the solubility of the

alloy. Some authors also fabricated and studied the permeability of PdCuAg alloys by different methods: electroless plating [243–245], magnetron sputtering [213,234], electrodeposition [246] and metallurgical [247]. Small additions of silver (1 at%) to fcc-PdCu alloys resulted in a great enhancement of hydrogen permeability. However with increasing silver quantities permeability decreases, but always maintaining a higher value than the binary PdCu [213]. L.M. Cornaglia group obtained hydrogen permeability values for the PdCuAg alloy similar to values of bcc-PdCu reported in literature, corresponding with values of permeation 2-3 times higher than fcc-PdCu, with high selectivity and good thermal stability up to 400°C [244]. However, surface co-segregation of both metals to the near-surface region was reported at moderate annealing conditions [243]. Zhao et al. studied PdCuAg with fcc structure with Cu contents ranging between 8.9 to 15.6 at% [245]. Although the permeability values shown in Table 8 are good, it is important to keep in mind that even though hydrogen permeability can be doubled with copper contents up to 10% compared to a $Pd_{70}Cu_{30}$ alloy, such small additions of copper will not be as effective against sulfur poisoning as higher copper content alloys [234]. So in this case the gain in hydrogen permeability is not worth against the loose of poisoning resistance. Nayebossadri et al. studied the addition of small amounts of silver (2.3-3.9 at%) to bcc-PdCu forming bcc and mixed (fcc+bcc) structures [247], with enhanced permeability compared to fcc-PdCu and analyzed the effects on solubility and diffusivity depending on the structure.

Gold addition has been studied to increase PdCu permeability fabricated by electroless plating [248,249], magnetron sputtering [213,250,251], electrodeposition [252] or mechanical alloying [253]. Tarditi et al. [249] analyzed electroless plated membranes with fcc structures upon exposure to 100 ppm of H_2S for 24h, reporting around 55% of flux reduction for various membrane compositions. They also demonstrated that replacing copper with gold with constant palladium content increase hydrogen permeability. Coulter et al. modeled and fabricated PdCuAu membranes with ffc structure and Cu composition ranging between 9 and 41 at% and gold between 4 and 9 at% [250]. Modelization results agree with experimental values of permeability of PdCu binary alloys, but for PdAu alloys model values are depressed in comparison with the experimental results. Permeation results collected in Table 8, show that Au addition does not make a great deal in improving the permeability of the alloys with higher Cu contents. Honrado Guerreiro et al. [253] prepared bcc-PdCuAu membranes by ball-mining metal powders with NaCl as process control agent. While under pure hydrogen conditions values of permeability are improved more than 30% compared with pure palladium, permeability on the presence of H_2S is greatly reduced due to segregation of copper and sulfur binding to the surface. Also, due to the presence of NaCl on the alloy, sodium segregation and formation of salts were also detected on the alloy surface.

PdCuNi alloy membranes have been developed in South Korea, deposited by magnetron sputtering and a Cu reflux process [254–259], using porous nickel supports (PNS) developed and manufactured by themselves [69,70]. The Cu reflux technique allowed

the production of a defect-free sputtered film and a great enhancement of the selectivity. Optimizing the pre-treatment of the support, they achieved hydrogen permeability values similar to pure Pd membranes with infinite selectivity [259] and excellent thermal stability and durability [257]. This material also exhibited excellent thermal cyclability, that is believed to be caused by the stabilization of the α phase in a wide range of temperatures.

A recent communication by Nayebossadri et al. [260] reported that small addition of zirconium (2 at%) improved the resistance of fcc-PdCu to the sulfur poisoning. Zr is thought to retard the surface segregation of Pd and Cu and hence slow down sulphide formation kinetics. In fact, $PdCu_{37}Zr_2$ (at%) ternary alloy exhibits 15% less reduction of hydrogen flow compared to $PdCu_{35}$ when exposed to hydrogen with 1000 ppm H_2S at 450 °C.

3.3. Other ternary and multicomponent alloys

With the objective of finding materials with improved poisoning resistance and long-thermal stability, platinum-group metals such as Pt [173] and Ru [261] have been used as alloying elements for PdAu alloys and fabricated using magnetron sputtering. Pd-Au-Pt permeability, with concentrations of Pt ranging from 4.3 to 12.9 wt%, is slightly below pure Pd values, as shown in Table 9. Experiments with WGS mixtures containing 20 ppm of H_2S showed good results, reporting a flux reduction of 50% and no sulfur compound formation. After H_2S exposure, pure hydrogen permeation is almost recovered to initial

values. However, long term exposure to H_2S appears to cause membrane degradation. On the other hand, Pd-Au-Ru is found to be less tolerant to H_2S than Pd-Au-Pt or PdAu, but shows acceptable values of hydrogen permeability and resistance to WGS gases with good thermal stability up to 450 ºC.

According to the results shown in section 2.5., palladium alloys with rare earths improve hydrogen permeability in comparison with pure palladium but also results in membrane hardening that can cause mechanical failure and corrosion enhancement. In order to overcome these issues, Sakamoto et al. have studied ternary based palladium-rare earth alloys, such as Pd-Y-Ag, Pd-Gd-Ag [208], Pd-Y-In, Pd-Y-Sn and Pd-Y-Pb [221] prepared using metallurgical methods. They performed crystallographic studies of these novel ternary systems and studied the alloy compositions that form a single homogeneous phase. $Pd_{100-x-y}(Y, Gd)_xAg_y$ with silver content up to 24% and satisfying the condition $y+3x \leq 24$, forms a single α phase [262] while $Pd_{100-x-y}Y_xIn_y$, has to satisfy $1.25x+y = 10$ and for $Pd_{100-x-y}Y_x(Sn, Pb)_y$, the composition condition changes to $1.125x+y = 9$ [263]. Membrane permeability in pure hydrogen of Pd(Y, Gd)Ag is higher comparing to a standard PdAg alloy, so it was assumed that it was caused by crystal lattice expansion due to the presence of rare earths, but permeability values of PdY and PdGd could not be improved by the addition of silver. Due to the positive results of this study the research group tried to improve the PdY alloy with atoms that allegedly caused crystal lattice expansion such as In, Sn and Pb. Results show that hydrogen permeability is considerably worse compared to the previous studies using silver additions. Table 9 shows that permeability

values are lowered up to 3% contents of In, Sn or Pb but with contents higher than 3% dramatic permeability losses are reported. Further studies are focused on the evaluation of poisoning resistance of these alloys, analyzing carbon monoxide [264], methane, ethylene [265] and ammonia [266] impurities in the hydrogen feed. Hydrogen permeability reduction due to poisoning for the Pd-Y(Gd)Ag alloy series are larger than those for the other alloys in CO and NH_3, while hydrocarbons seem to have no poisoning effect at all.

In the USSR, there has been an extensive work in the research of binary, ternary and higher palladium alloys, but almost none of the studies are published in English. In one of the few articles that have been sent to journals in English, Burkhanov et al. [34] published a review in which they claim that $PdIn_6Ru_{0.5}$ is the best silver-free alloy they had found due to its good combination of mechanical properties, permeability and corrosion resistance. This alloy has also been included in a review made by Gryaznov [13], where it is also included the comparison of binary and ternary alloys with pure palladium fabricated in several Moscow institutes with enhanced permeability values. In a recent article, Didenko et al. [267], reported a permeability 3 times higher than $PdAg_{23}$ alloy and an insignificant negative effect of CO in the gas mixture for $PdIn_6Ru_{0.5}$. Multicomponent PdAg-based and PdPt-based alloys called 'B type' were developed in the former USSR during the 1970s [268]. PdAg and PdPt were chosen as basecase binary systems for membrane material development in combination with elements such as In, V, Ag, Ti, Mo, W, Rh, Nb or B [269]. Among all the multicomponent alloys prepared, the

B-1, whose composition is 80.6Pd-15Ag-3Au-0.6Pt-0.6Ru-0.2Al (wt%), was found to be the best on the basis of PdAg system, while B-11, 79.5Pd-15Pt-5Rh-0.5Y (wt%), was the best on the basis of PdPt system [270]. These series of membranes were prepared by melting of the high-purity components. The B-1 alloy was used in industry due to its optimum characteristics: strength, plasticity and corrosion-resistance in hydrocarbon gas media [34]. B-11 was found to be an excellent candidate for gas separation above 600ºC, presenting an excellent thermal cyclability.

4. Computational methods: The next step on alloy search

Density functional theory (DFT) is a computational modeling method used to investigate the electronic structure of condensed phases and is the most popular and successful method available in condensed-matter physics, computational physics, and computational chemistry. This method gives an approximate solution to the Schrödinger equation of a many-body system, calculating approximate functionals, i.e. functions of a function of the spatially dependent electron density. DFT-based methods can be quite useful to accelerate the discovery and optimization of materials when a large amount of elements and compositions are required to be screened. For Pd-based membranes, DFT calculations can be used for any atom configuration of periodic table elements, obtaining ground state electronic values that are used to predict solution-diffusion mechanism in the metals. Most of the research in DFT material screening for Pd-based dense metallic membranes has been conducted by the group of David S. Sholl [271,272].

This group suggested five principles that should be taken into account in any application for material screening, as written in [273]: (i) Theoretical predictions must be made for multiple materials on time scales shorter than the same materials can be assessed experimentally. (ii) Theoretical predictions should require minimal input from experimental data. (iii) Theoretical predictions must be made about the quantities relevant to end-use applications, i.e. macroscopic properties. (iv) Theoretical predictions need to have sufficient quantitative accuracy that confident judgments can be made separating promising and unpromising materials. (v) The assumptions and caveats associated with theoretical methods should be clearly stated to allow judgments to be made about the potential impact of these factors on 'real world' performance of materials.

Kamakoti and Sholl developed a method to calculate solubility, diffusivity and permeability of hydrogen in PdCu alloys without any experimental data input [158,274,275]. Since then, similar methods have been used in first principle calculations for PdAg and PdAu [170,276,277] and also amorphous metals [273]. Besides hydrogen permeability, these methods have also been used to calculate the effect of H_2S on Pd and Pd-based alloys [23,41,220,233,278], the surface segregation effects of the alloys [48,49,54,233] and surface resistance to hydrogen transport [279]. One of the most important challenges to overcome in order to achieve a good description of permeation properties on crystalline alloys is the frequent substitutional disorder of the metal atoms. Cluster expansion (CE) methods, that use interstitial site binding and transition-

state energies libraries, have been used to develop a lattice model for bulk properties to overcome this issue. CE methods have been used to calculate hydrogen permeabilities of $Pd_{96}M_4$ alloys, where M = Ag, Au, Pt, Rh, Cu, and Ni [280]. Later studies extended the CE calculations to fcc $Pd_{96}M_4$ alloys with transition metals that form solid solutions with Pd at 600K [209]. Pd-based intermetallic alloys have discrete and ordered compositions, that can potentially improve the resistance to poisoning due to the enhanced thermodynamic stabilities compared to the disordered solid solutions, have also been screened using DFT methodologies [281].

While binary alloy permeability predictions using DFT are already well defined, ternary alloy studies are still being developed. For now, they are focused on PdCu-based ternary alloys, as mentioned previously in this review, to use binary PdCu sulfur resistance combined with another element that can improve the hydrogen permeability. The initial articles studied small additions (4 at%) of several transition metals to the binary alloy [239,240]. Later studies examined hydrogen permeability for a broad range of ternary compositions of PdCuAg [242] and PdCuAu [248]. With the knowledge acquired in the study of binary alloys, theoretical predictions for hydrogen permeability in ternary alloys have proved to be a powerful tool for membrane material screening and might be the tool that bumps Pd-based membrane research to a new step.

5. Conclusions

Membranes based on palladium alloys are a technology with great expectations for hydrogen purification in the near future, their low permeability compared to other membrane materials is compensated by a potential infinite selectivity and no associated energy costs of the separation. The use of supports was first introduced 25 years ago, and since then, new fabrication methods have allowed big reductions in the palladium film thickness, increasing the permeability of the metal foils used before. Two fabrication methods emerged as the most used and widespread for supported membrane manufacture: electroless plating and magnetron sputtering. Among them, electroless plating can be considered the best deposition method for industrial preparation due to the low price of the technique, the easy scaling up and the ability to make films in non-planar surfaces.

In this paper, a systematic review of the different alloying elements used in combination with palladium is presented and discussed, aiming to give the readers the chance of a quick overview of the research over the years in palladium-based membrane technology, along with permeability data from the original articles. However, a significant technical barrier impeding the industrial application of Pd based membranes is the susceptibility of Pd containing membranes to poisoning or corrosion by components present in gasifier effluent streams. Even though some alloys are resistant to poisoning, reduction of permeability in the presence of some gases, specially H_2S, is still quite important and must require further research. We expect that this review will

stimulate additional research in this field leading to a future industrial implantation of the technology.

Optimization of the alloys and the fabrication methods are a fundamental piece on the advance of Pd-based membranes, but as it is shown in the introduction, there are many other factors to take into account when using membranes in order to achieve a proper efficiency in membrane operation. Special attention must be paid to supports (porosity, smoothness and adhesion), microstructure of the film and activation methods. Also other metallurgical aspects of the alloy, such as segregation should be taken into account, in order to optimize the performance of a certain alloy.

Finally, advances in computational methods have proven DFT analysis to be a useful tool to point out and narrow down promising alloys for its use as hydrogen purification membranes. We expect that the introduction of this technique will speed-up the advances on membrane materials and lead to better alloys reducing the time to test membrane composition and alloying elements by trial and error.

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Table 1. Hydrogen permeabilities in pure hydrogen of Pd-Ag binary alloys

Alloy (at%)	Support	Thickness (μm)	Prep. method	Permeability (10^{-8} mol·m^{-1}·s^{-1}·Pa$^{-0.5}$)	T (°C)	P_{alloy}/P_{Pd}	Ref.
$PdAg_{11}$ [a]	Al_2O_3	5.0	ELP	0.90	400	1.36	[123]
$PdAg_{18}$ [a]	Al_2O_3	5.3	ELP	1.07	400	1.62	
$PdAg_{23}$ [a]	Al_2O_3	5.8	ELP	1.22	400	1.85	
$PdAg_{26}$ [a]	Al_2O_3	5.9	ELP	0.97	400	1.47	
$PdAg_{31}$ [a]	Al_2O_3	6.4	ELP	0.84	400	1.27	
$PdAg_{5}$ [a]	Al_2O_3	4.5	ELP	0.54	300	1.09	[127]
$PdAg_{10}$ [a]	Al_2O_3	4.5	ELP	0.86	300	1.75	
$PdAg_{15}$ [a]	Al_2O_3	4.5	ELP	0.96	300	1.84	
$PdAg_{20}$ [a]	Al_2O_3	4.5	ELP	0.65	300	1.31	
$PdAg_{23}$ [a]	Al_2O_3	4.5	ELP	0.84	300	1.69	
$PdAg_{13}$ [a]	Inconel	8.3	ELP	1.13	550	-	[132]
$PdAg_{20}$ [a]	Inconel	9.4	ELP	1.83	550	-	
$PdAg_{31}$ [a]	Inconel	8.9	ELP+Electrodep	1.56	550	-	
$PdAg_{24}$ [a]	PSS/Al_2O_3	20	ELP	1.82	450	-	[133]
$PdAg_{25}$ [a]	PSS/Al_2O_3	18	ELP	1.75	450	-	
$PdAg_{26}$ [a]	PSS/NaA	20	ELP	1.12	450	-	
$PdAg_{10}$	PSS/ZrO_2	-	ELP	1.65	400	1.36	[235]
$PdAg_{25}$	Al_2O_3	0.2	Mag. sputtering	0.6 [b]	400	-	[93]
$PdAg_{23}$ [a]	Si_3N_4	0.8	Mag. sputtering	19 [b]	400	-	[98]
$PdAg_{23}$ [a]	SS plate	1.3	Mag. sputtering	2.21	300	-	[118]
$PdAg_{23}$ [a]	SS plate	2.8	Mag. sputtering	3.2	400	-	[119]
$PdAg_{23}$ [a]	SS plate	2.2	Mag. sputtering	1.3	450	1.55	[139]
$PdAg_{10}$ [a]	Self-sup	-	Metallurgical	-	500	1.5	[13]
$PdAg_{20}$ [a]	Self-sup	-	Metallurgical	-	500	1.6	
$PdAg_{30}$ [a]	Self-sup	-	Metallurgical	-	500	1.8	
$PdAg_{40}$ [a]	Self-sup	-	Metallurgical	-	500	1.8	
$PdAg_{25}$	Self-sup	100	Metallurgical	2.43	400	-	[202]
$PdAg_{24}$	Self-sup	700	Metallurgical	2.31	350	2.10	[208]

[a] wt%, [b] n=1

Table 2. Hydrogen permeabilities in pure hydrogen of Pd-Cu binary alloys

Alloy (at%)	Support	Thickness (μm)	Prep. method	Permeability (10^{-8} mol·m^{-1}·s^{-1}·Pa$^{-0.5}$)	T (°C)	P_{alloy}/P_{Pd}	Ref.
$PdCu_{53}$	Self-sup	25	Metallurgical	1.17	350	1.17	[24]
$PdCu_{40}$ [a]	Self-sup	20-50	Metallurgical	2.04	400	1.63	[34]
$PdCu_{55}$ [a]	Self-sup	~1000	Metallurgical	0.24	400	0.21	[145]
$PdCu_{57}$ [a]	Self-sup	~1000	Metallurgical	0.66	400	0.59	
$PdCu_{60}$ [a]	Self-sup	~1000	Metallurgical	1.52	400	1.36	
$PdCu_{63}$ [a]	Self-sup	~1000	Metallurgical	0.98	400	0.88	
$PdCu_{70}$ [a]	Self-sup	~1000	Metallurgical	0.11	400	0.10	
$PdCu_{90}$ [a]	Self-sup	~1000	Metallurgical	0.64	400	0.57	
$PdCu_{6}$ [a]	Vycor	18.9	ELP	0.27	400	-	[65]
$PdCu_{9}$ [a]	Al_2O_3/ZrO_2	12.0	ELP	2.75	500	-	[146]
$PdCu_{19}$ [a]	Al_2O_3	11.6	ELP	1.73	500	-	
$PdCu_{22}$ [a]	Al_2O_3	12.5	ELP	0.64	450	-	
$PdCu_{40}$ [a]	Al_2O_3/ZrO_2	1.5	ELP	0.57	350	-	
$PdCu_{10}$ [a]	Al_2O_3/ZrO_2	1.0	ELP	0.075	350	-	[162]
$PdCu_{30}$ [a]	Al_2O_3/ZrO_2	1.5	ELP	0.25	350	-	
$PdCu_{40}$ [a]	Al_2O_3/ZrO_2	1.5	ELP	0.57	350	-	
$PdCu_{90}$ [a]	Al_2O_3/ZrO_2	2.5	ELP	0.0008	350	-	
$PdCu_{16}$	PSS/ZrO_2	5	ELP	0.21	400	-	[163]
$PdCu_{41}$ [a]	PSS/Al_2O_3	16.7	ELP	1.33	400	≈1	[164]

$PdCu_{36}$	Al_2O_3	4	ELP	0.16	450	-	[154]
$PdCu_{30}$	Al_2O_3	5.5	ELP	0.25	350	-	[166]
$PdCu_{42}$	Al_2O_3	7.0	ELP	0.07	350	-	
$PdCu_6$	SS plate	2.2	Mag. sputtering	0.84 [b]	400	0.84	[213]
$PdCu_{17}$	SS plate	1.7	Mag. sputtering	0.50 [b]	400	0.50	
$PdCu_{30}$	SS plate	2.1	Mag. sputtering	0.38 [b]	400	0.38	
$PdCu_{40}$	SS plate	2.1	Mag. sputtering	0.20 [b]	400	0.20	
$PdCu_{53}$	SS plate	2.2	Mag. sputtering	0.84 [b]	400	0.84	

[a] wt%, [b] Permeation gas: H_2/10% N_2

Table 3. Hydrogen permeabilities in pure hydrogen of Pd-Au binary alloys

Alloy (at%)	Support	Thickness (μm)	Prep. method	Permeability (10^{-8} mol·m^{-1}·s^{-1}·Pa$^{-0.5}$)	T (°C)	P_{alloy} / P_{Pd}	Ref.
$PdAu_5$ [a]	Self-sup	-	Metallurgical	-	500	2.0	[13]
$PdAu_{10}$ [a]	Self-sup	-	Metallurgical	-	500	2.2	
$PdAu_{15}$ [a]	Self-sup	-	Metallurgical	-	500	2.1	
$PdAu_{20}$ [a]	Self-sup	-	Metallurgical	-	500	2.0	
$PdAu_9$	Self-sup	100-150	Metallurgical	2.18	300	1.10	[169]
$PdAu_{12}$	Self-sup	100-150	Metallurgical	2.21	300	1.12	
$PdAu_{19}$	Self-sup	100-150	Metallurgical	1.95	300	0.98	
$PdAu_{21}$	Self-sup	100-150	Metallurgical	1.72	300	0.87	
$PdAu_{26}$	Self-sup	100-150	Metallurgical	1.29	300	0.65	
$PdAu_{30}$	Self-sup	100-150	Metallurgical	0.80	300	0.40	
$PdAu_{35}$	Self-sup	100-150	Metallurgical	0.35	300	0.18	
$PdAu_5$ [a]	Self-sup	25	Metallurgical	1.37	400	0.98	[171]
$PdAu_{10}$ [a]	Self-sup	25	Metallurgical	1.35	400	0.96	
$PdAu_{15}$ [a]	Self-sup	25	Metallurgical	1.33	400	0.95	
$PdAu_{20}$ [a]	Self-sup	25	Metallurgical	1.50	400	1.07	
$PdAu_{40}$ [a]	Self-sup	25	Metallurgical	0.78	400	0.56	
$PdAu_{10}$ [a]	PSS/Al_2O_3	25	Metallurgical	1.16	400	-	[179]
$PdAu_{19}$ [a]	PSS/Al_2O_3	25	Metallurgical	1.00	400	-	
$PdAu_5$ [a]	Self-sup	8	Mag. sputtering	1.67	400	-	[171]
$PdAu_{10}$ [a]	Self-sup	12	Mag. sputtering	1.65	400	-	
$PdAu_{10}$ [a]	PSS/Al_2O_3	24	Mag. sputtering	1.56	400	1.33	[173]
$PdAu_5$	SS plate	2.5	Mag. sputtering	1.1 [b]	400	1.13	[213]
$PdAu_{15}$	SS plate	1.9	Mag. sputtering	0.76 [b]	400	1.17	[139]
$PdAu_8$ [a]	Inconel	18.1	ELP	0.48	500	0.13 [c]	[172]
$PdAu_4$ [a]	Al_2O_3	4-5	ELP	0.7	400	-	[174]
$PdAu_5$	Al_2O_3	5	ELP	1.3	400	-	[177]
$PdAu_{2.5}$ [a]	PSS/Al_2O_3	9.1	ELP	0.67	400	0.50	[178]
$PdAu_4$ [a]	PSS/Al_2O_3	5.4	ELP	1.11	400	0.82	
$PdAu_9$ [a]	PSS/Al_2O_3	10.3	ELP	0.69	400	0.51	
$PdAu_{11.5}$ [a]	PSS/Al_2O_3	13	ELP	0.45	400	0.31	
$PdAu_{13}$ [a]	PSS/Al_2O_3	13	ELP	0.41	400	0.30	
$PdAu_9$	PSS/ZrO_2	-	ELP	0.99	400	0.82	[235]

[a] wt%, [b] Permeation gas: H_2/10% N_2, [c] Support intermetallic diffusion

Table 4. Hydrogen permeabilities in pure hydrogen of Pd-Pt group metals binary alloys

Alloy (at%)	Support	Thickness (μm)	Prep. method	Permeability (10^{-8} mol·m^{-1}·s^{-1}·Pa$^{-0.5}$)	T (°C)	P_{alloy} / P_{Pd}	Ref.
$PdRu_6$ [a]	Self-sup	20-50	Metallurgical	1.12	400	0.89	[34]
$PdRu_5$ [a]	AccuSep®	2.9	ELP	1.28	450	-	[184]
$PdRu_{10}$ [a]	AccuSep®	4.5	ELP	1.30	450	-	
$PdRu_{0.5}$ [a]	AccuSep®	6.0	ELP	1.26	550	1.08	[185]
$PdRu_{0.5}$ [a]	PSS/Al_2O_3	22	ELP	0.65	400	-	[186]

$PdRu_3$ [a]	PSS/Al_2O_3	5.8	ELP	1.28	450	0.99	[187]
$PdRu_5$ [a]	PSS/Al_2O_3	7.8	ELP	1.31	450	1.01	
$PdRu_8$ [a]	PSS/Al_2O_3	6.4	ELP	1.28	450	0.98	
$PdRu_{11}$ [a]	PSS/Al_2O_3	5.6	ELP	1.16	450	0.90	
$PdRu_5$	SS plate	2.2	Mag. sputtering	0.82[c]	400	0.81	[213]
Pd/Ru [b]	PHA/Al_2O_3	6.8	ELP	2.3	500	1.40	[195]
$PdPt_{17}$ [a]	AccuSep®	6.4	ELP	0.67	550	0.75	[185]
$PdPt_{27}$ [a]	AccuSep®	3.9	ELP	0.39	550	0.33	
$PdPt_5$ [a]	YSZ	6.5	ELP	0.78	450	0.86	[197]
$PdPt_9$ [a]	YSZ	6.7	ELP	0.55	450	0.61	
$PdPt_{26}$ [a]	YSZ	11.4	ELP	0.29	450	0.32	
$PdPt_{31}$	Self-sup	100	Metallurgical	1.00	650	0.33	[199]
$PdRh_4$ [a]	α-Al_2O_3	13.5	ELP	1.3	450	-	[200]
$PdRu_5$ [a]	Self-sup	-	Metallurgical	-	500	1.4	[13]
$PdPt_{10}$ [a]	Self-sup	-	Metallurgical	-	500	1.2	
$PdPt_{20}$ [a]	Self-sup	-	Metallurgical	-	500	0.6	
$PdRh_5$ [a]	Self-sup	-	Metallurgical	-	500	1.4	
$PdRh_{10}$ [a]	Self-sup	-	Metallurgical	-	500	0.9	

[a] wt%, [b] Composite membrane (non-alloy), [c] Permeation gas: H_2/10% N_2

Table 5. Hydrogen permeabilities in pure hydrogen of Pd-rare earth binary alloys

Alloy (at%)	Support	Thickness (μm)	Prep. method	Permeability (10^{-8} mol·m^{-1}·s^{-1}·Pa$^{-0.5}$)	T (°C)	P_{alloy} / P_{Pd}	Ref.
PdY_7 [a]	Self-sup	20-50	Metallurgical	5.12	400	4.09	[34]
$PdY_{6.6}$	Self-sup	100	Metallurgical	5.39	350	1.68[c]	[205]
PdY_{10}	Self-sup	100	Metallurgical	5.69	350	1.77[c]	
PdY_8	Self-sup	100	Metallurgical	6.47	400	2.70[c]	[202]
PdY_8	Self-sup	700	Metallurgical	3.92	350	3.57	[208]
PdY_5	SS plate	2.0	Mag. sputtering	1.10[b]	400	1.13	[213]
$PdGd_8$	Self-sup	100	Metallurgical	5.15	400	2.14[c]	[202]
$PdGd_8$	Self-sup	700	Metallurgical	5.33	350	4.86	[208]
$PdCe_{5.7}$	Self-sup	100	Metallurgical	2.60	400	1.08[c]	[202]
$PdTm_7$ [a]	PSS/Al_2O_3	33.6	Mag. sputtering	2.57	400	1.77	[209]

[a] wt%, [b] Permeation gas: H_2/10% N_2, [c] Compared to $Pd_{75}Ag_{25}$

Table 6. Hydrogen permeabilities in pure hydrogen of other Pd-based binary alloys

Alloy (at%)	Support	Thickness (μm)	Prep. method	Permeability (10^{-8} mol·m^{-1}·s^{-1}·Pa$^{-0.5}$)	T (°C)	P_{alloy} / P_{Pd}	Ref.
$PdIn_{10}$	Self-sup	700	Metallurgical	1.06	350	0.97	[221]
$PdSn_9$	Self-sup	700	Metallurgical	0.73	350	0.66	
$PdPb_9$	Self-sup	700	Metallurgical	1.46	350	1.33	
$PdMo_5$	SS plate	1.9	Mag. sputtering	0.50[a]	400	0.49	[213]
$PdTa_5$	SS plate	1.8	Mag. sputtering	0.52[a]	400	0.51	
$PdNb_5$	SS plate	2.0	Mag. sputtering	0.83[a]	400	0.82	
$PdNb_{0.3}$	PSS/Ni	1-2	CVD	0.28	450	0.17	[214]
$PdNi_{22}$	PSS/Ni	1	Electrodeposit.	0.40[b]	450	-	[114]
$PdNi_{20}$	PSS/Ni	2	Electrodeposit.	0.65[b]	450	-	[115]
$PdNi_{29}$	PSS/Ni	2	Electrodeposit.	0.24[b]	450	-	
$PdNi_{0.2\text{-}0.3}$	PSS/Ni	1-2	CVD	0.59	450	0.36	[214]
$PdNi_5$	Al_2O_3	1-2	ELP	0.27[b]	450	-	[223]
$PdAl_{0.02}$	Self-sup	132	Metallurgical	1.26	200	0.80	[225]
$PdAl_{0.06}$	Self-sup	115	Metallurgical	0.54	200	0.43	
$PdFe_{0.04}$	Self-sup	-	Metallurgical	0.61	200	0.54	[227]
$PdFe_{0.1}$	Self-sup	-	Metallurgical	0.09	200	0.15	
$PdFe_7$	PSS	6	Electrodeposit.	0.65	200	-	[113]

$PdFe_{19}$	PSS	11	Electrodeposit.	0.22	200	-	

[a] Permeation gas: H_2/10% N_2, [b] n=1

Table 7. Hydrogen permeabilities in pure hydrogen of PdAg-based ternary alloys

Alloy (at%)	Support	Thick. (μm)	Prep. method	Permeability (10^{-8} mol·m^{-1}·s^{-1}·Pa$^{-0.5}$)	T (°C)	P_{alloy} / P_{Pd}	P_{alloy} / P_{PdAg}	Ref.
$PdAg_{11}Cu_4$	SS plate	2.2	Mag. sputtering	0.78[b]	400	-	0.65	[234]
$PdAg_{22}Au_3$	SS plate	1.9	Mag. sputtering	0.85[b]	400	-	0.71	
$PdAg_{27}Y_4$	SS plate	2.4	Mag. sputtering	1.10[b]	400	-	0.92	
$PdAg_{21}Mo_3$	SS plate	2.3	Mag. sputtering	0.50[b]	400	-	0.42	
$PdAg_2Au_{15}$	PSS/ZrO_2	14	ELP	1.2	400	1.08	-	[235]
$PdAg_{16}Au_9$	PSS/ZrO_2	14	ELP	1.21	400	0.98	0.73	[236]
$PdAg_9Au_{13}$	PSS/ZrO_2	14	ELP	1.34	400	1.10	0.79	
$PdAg_{13}Au_{20}$ [a]	AccuSep®	9.3	ELP	1.32	400	-	-	[237]
$PdAg_{30}Ru_1$ [a]	Al_2O_3	5	ELP	3.55	450	3-4	-	[238]
$PdAg_{30}Ru_2$ [a]	Self-sup	-	Metallurgical	-	500	2.2	-	[13]
$PdAg_{19}Rh_1$ [a]	Self-sup	-	Metallurgical	-	500	2.6	-	

[a] wt%, [b] Permeation gas: H_2/10% N_2

Table 8. Hydrogen permeabilities in pure hydrogen of PdCu-based ternary alloys

Alloy (at%)	Support	Thick. (μm)	Prep. method	Permeability (10^{-8} mol·m^{-1}·s^{-1}·Pa$^{-0.5}$)	T (°C)	P_{alloy} / P_{Pd}	P_{alloy} / P_{PdCu}	Ref.
$PdCu_{20}Ag_6$	SS plate	2.1	Mag. sputtering	0.44	400	0.44	1.33	[213]
$PdCu_{29}Ag_{13}$	SS plate	2.0	Mag. sputtering	0.27	400	0.27	0.82	
$PdCu_{21}Ag_{14}$	SS plate	2.1	Mag. sputtering	0.47	400	0.47	1.42	
$PdCu_{27}Au_1$	SS plate	2.1	Mag. sputtering	0.42	400	0.42	1.27	
$PdCu_{25}Au_3$	SS plate	2.1	Mag. sputtering	0.38	400	0.38	1.15	
$PdCu_{26}Ru_4$	SS plate	1.7	Mag. sputtering	0.22	400	0.22	0.67	
$PdCu_{24}Mo_1$	SS plate	1.8	Mag. sputtering	0.35	400	0.35	1.06	
$PdCu_{26}Mo_4$	SS plate	2.2	Mag. sputtering	0.14	400	0.14	0.42	
$PdCu_{26}Ta_1$	SS plate	1.8	Mag. sputtering	0.45	400	0.44	1.36	
$PdCu_{26}Ta_4$	SS plate	1.8	Mag. sputtering	0.32	400	0.32	0.97	
$PdCu_{26}Y_1$	SS plate	2.2	Mag. sputtering	0.52	400	0.51	1.57	
$PdCu_{22}Y_1$	SS plate	1.8	Mag. sputtering	0.50	400	0.49	1.51	
$PdCu_{25}Ag_7$	PSS	25	ELP	0.54	450	0.36	-	[244]
$PdCu_9Ag_{20}$	Al_2O_3	4.4	ELP	0.80	400	-	-	[245]
$PdCu_5Ag_{19}$	Al_2O_3	3.8	ELP	0.85	400	-	-	
$PdCu_{11}Ag_{14}$	Al_2O_3	2.5	ELP	0.50	400	-	-	
$PdCu_{11}Ag_{10}$	Al_2O_3	4.6	ELP	1.23	400	-	-	
$PdCu_{11}Ag_5$	Al_2O_3	3.5	ELP	0.62	400	-	-	
$PdCu_{16}Ag_4$	Al_2O_3	3.3	ELP	0.40	400	-	-	
$PdCu_{51}Ag_4$	Self-sup	35	Metallurgical	1.33	400	-	0.71	[247]
$PdCu_{52}Ag_2$	Self-sup	40	Metallurgical	1.02	400	-	0.54	
$PdCu_{25}Au_5$	PSS/ZrO_2	14	ELP	0.19	400	0.16	-	[249]
$PdCu_{37}Au_3$	PSS/ZrO_2	14	ELP	0.29	400	0.24	-	
$PdCu_{14}Au_{17}$	PSS/ZrO_2	14	ELP	0.87	400	0.73	-	
$PdCu_{10}Au_7$	PSS	10	Mag. sputtering	0.8	350	-	0.79	[250]
$PdCu_{26}Au_2$	PSS	10	Mag. sputtering	0.3	350	-	0.29	
$PdCu_{41}Au_4$	PSS	10	Mag. sputtering	0.1	350	-	0.09	
$PdCu_{57}Au_3$	Self-sup	300	Metallurgical	1.6	464	1.00	1.07	[253]
$PdCu_{53}Au_7$	Self-sup	277	Metallurgical	2.1	464	1.31	1.40	
$PdCu_{49}Au_{11}$	Self-sup	304	Metallurgical	0.7	464	0.44	0.47	
$PdCu_7Ni_2$ [a]	PNS	12	Mag. sputtering	0.31 [c]	400	-	-	[256]

$PdCu_5Ni_7$ [a]	PNS	5	Mag. sputtering	0.30 [c]	400	-	-	
$PdCu_7Ni_4$ [a]	PNS	12	Mag. sputtering	0.91 [c]	400	-	-	[257]
$PdCu_{37}Zr_2$	Self-sup	112.5	Metallurgical	0.14	350	-	0.7	[260]

[a] wt%, [b] Permeation gas: H_2/10% N_2, [c] n=0.8-0.9

Table 9. Hydrogen permeabilities in pure hydrogen of other Pd-based ternary (or higher) alloys

Alloy (at%)	Support	Thick. (μm)	Prep. method	Permeability (10^{-8} mol·m^{-1}·s^{-1}·Pa$^{-0.5}$)	T (°C)	P_{alloy} / P_{Pd}	P_{alloy} / P_{PdCu}	Ref.
$PdAu_{11}Pt_4$ [a]	PSS/Al_2O_3	10	Mag. sputtering	0.63	400	0.54	0.40	[173]
$PdAu_{12}Pt_{11}$ [a]	PSS/Al_2O_3	25	Mag. sputtering	1.04	400	0.89	0.67	
$PdAu_{11}Ru_5$ [a]	PSS/ZrO_2	3.5	Mag. sputtering	1.68	500	-	-	[261]
$PdY_{6.3}Ag_5$	Self-sup	700	Metallurgical	4.24	350	3.87	0.98	[208]
PdY_3Ag_{15}	Self-sup	700	Metallurgical	3.35	350	3.05	0.79	
$PdGd_{6.3}Ag_5$	Self-sup	700	Metallurgical	5.66	350	5.17	0.97	
$PdGd_3Ag_{15}$	Self-sup	700	Metallurgical	3.52	350	3.21	0.60	
$PdY_6In_{2.5}$	Self-sup	700	Metallurgical	3.12	350	2.85	0.73	[221]
$PdY_2In_{7.5}$	Self-sup	700	Metallurgical	1.69	350	1.54	0.43	
$PdY_6Sn_{2.5}$	Self-sup	700	Metallurgical	2.76	350	2.52	0.64	
$PdY_{1.3}Sn_{7.5}$	Self-sup	700	Metallurgical	0.96	350	0.88	0.24	
$PdY_6Pb_{2.5}$	Self-sup	700	Metallurgical	3.46	350	3.16	0.81	
$PdY_{1.3}Pb_{7.5}$	Self-sup	700	Metallurgical	1.80	350	1.64	0.46	
$PdIn_6Ru_{0.5}$ [a]	Self-sup	20-50	Metallurgical	1.48	400	1.19	-	[34]
B-1	Self-sup	1000	Metallurgical	2.16	500	1.17	-	[270]
B-11	Self-sup	1000	Metallurgical	1.52	500	0.83	-	

[a] wt%

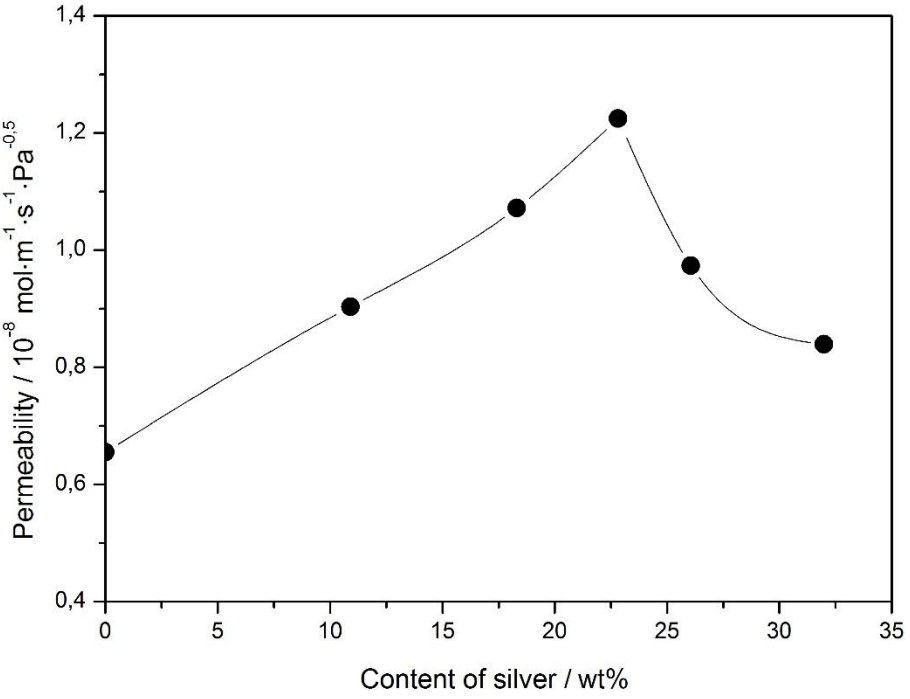

Fig. 1. Effect of the silver content on hydrogen permeation coefficient at 673K. Reprinted (and adapted) from Uemiya, S. et al. (1991) J. Membr. Sci. 56, 315-325. Copyright (1991), with permission from Elsevier.

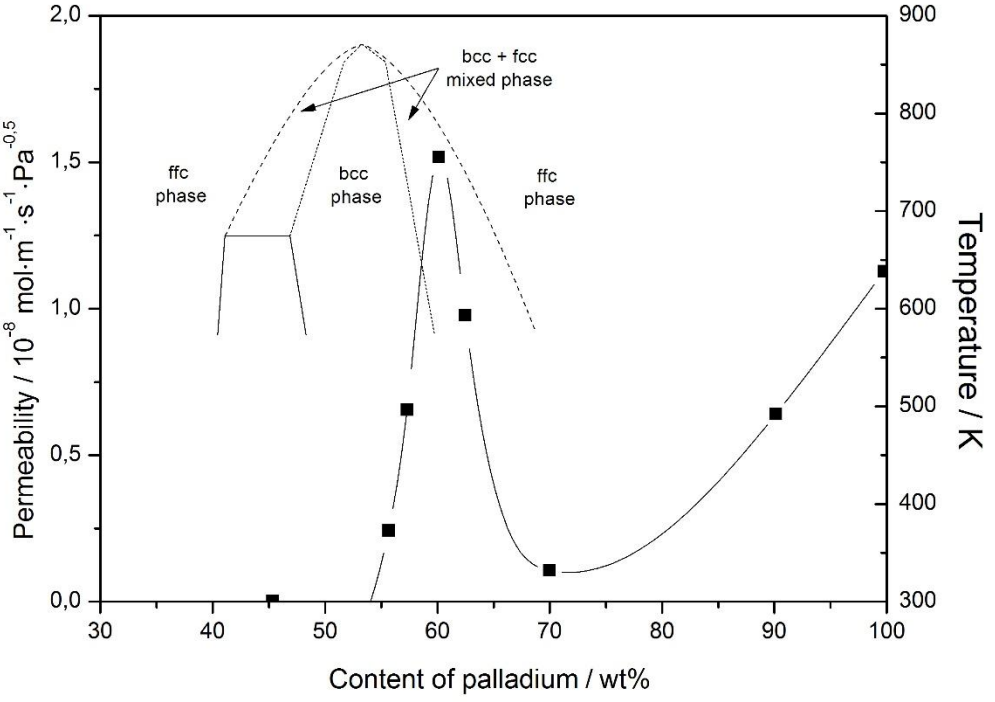

Fig. 2. Hydrogen permeability as a function of palladium wt% at 623 K and phase diagram of Pd-Cu alloys. Permeability data is taken from reference [145] and phase diagram data is taken from [153].

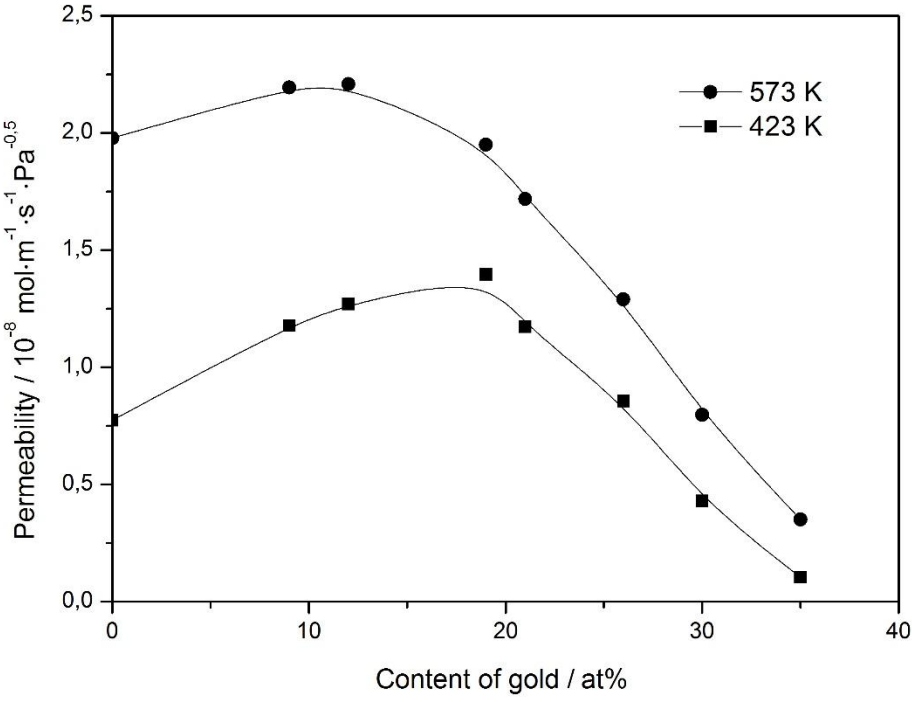

Fig. 3. Permeabilities as a function of gold atomic fraction at different temperatures. Reprinted (and adapted) with permission from Flanagan, T.B. and Wang, D. (2011) J. Phys. Chem. C 115, 11618-11623. Copyright (2011) American Chemical Society.

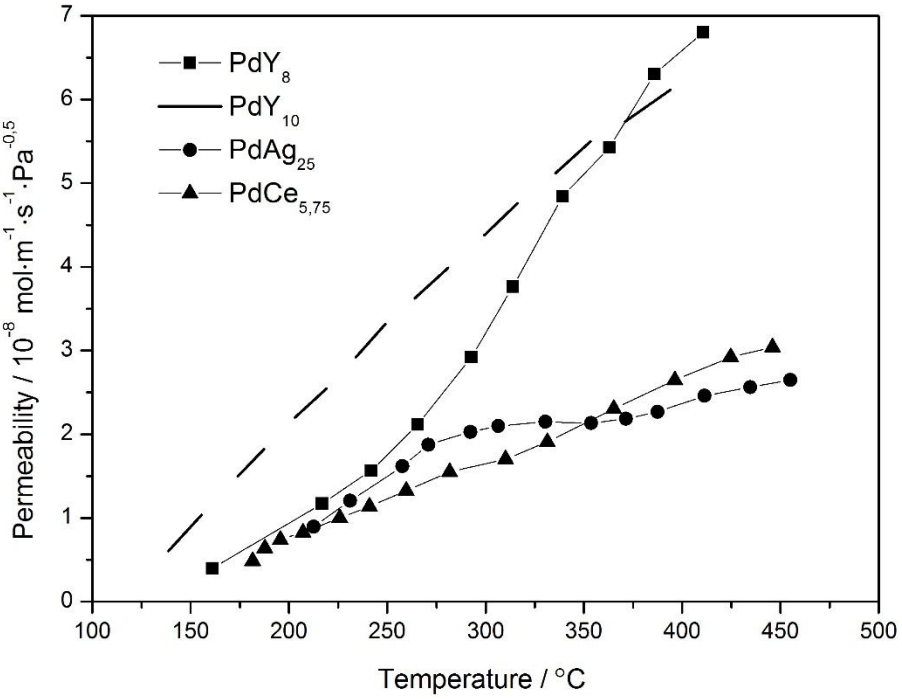

Fig. 4. Comparison of the permeabilities of Pd-rare earth with PdAg. Reprinted (and adapted) from Hughes, D.T. and Harris, I.R. (1978) J. Common Met. 61, 9-21. Copyright (1978), with permission from Elsevier.

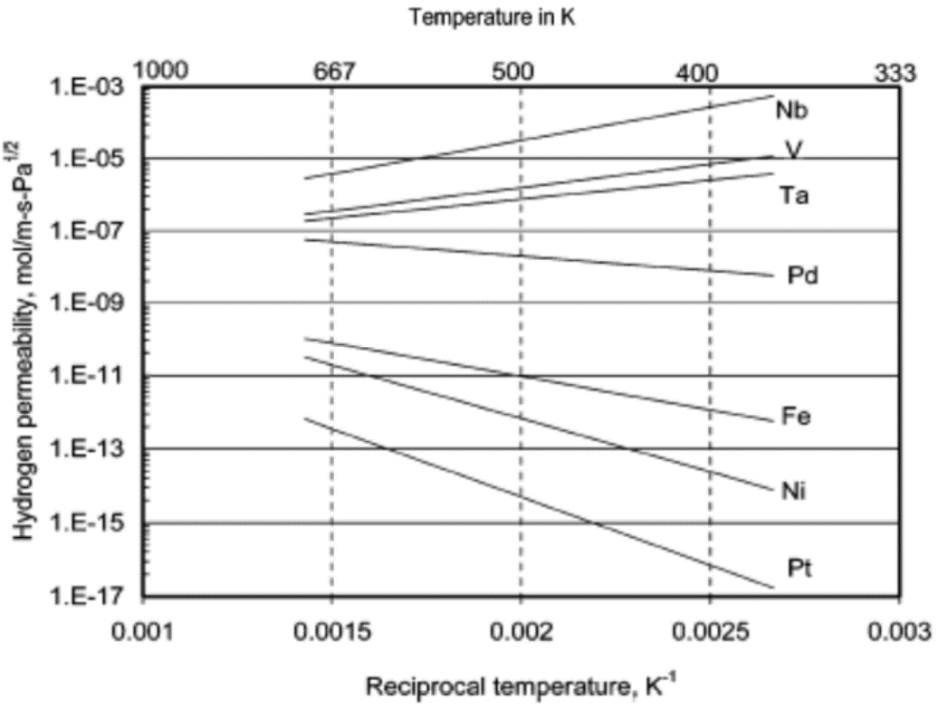

Fig. 5. Hydrogen permeability as a function of temperature for various metals. Reprinted with permission from Adhikari, S. and Fernando, S. (2006) Ind. Eng. Chem. Res. 45, 875-881. Copyright (2006) American Chemical Society.