

Chapter 2

Processing and Characterization of Coating and Thin Film Materials

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2.1 Introduction

Coatings and thin film materials are employed in many different industrial fields for decades, mainly for protective purposes. This large experience provokes that, currently, a wide variety of technologies for both preparation and characterization are available. Particularly, focusing on energy and environmental applications, three main film types can be distinguished: (1) materials with catalytic activity for hydrogen production, (2) membranes for hydrogen separation or CO₂ capture, and (3) coatings for some specific fuel cell components. Membranes are especially relevant for hydrogen separation from other gases after the production unit or combining both production and separation steps in a unique equipment, the membrane reactor. The last case represents a significant advance in terms of process intensification, increasing the hydrogen production rate with a high purity and saving costs. In the last years, the relevance of these membrane materials has significantly increased, as can be denoted by the large number of published manuscripts in indexed scientific journals of high impact. In this context, this chapter summarizes the main advances in thin film membranes towards energy and environmental applications, including both preparation strategies and the most common characterization techniques. The production of all these thin films, independently of the particular application, can be carried out by different physical-chemical alternatives such as Sol–Gel methods, Electrodeposition, Electroless Plating, Physical Vapor Deposition, Chemical Vapor Deposition, Atomic Layer Deposition, or Molecular Beam Epitaxy, achieving thicknesses ranged from the nanometer scale

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to some microns. Each technique presents advantages and disadvantages that have to be taken into account for final applications. Moreover, the structure of the film should also be considered, being possible to distinguish amorphous or crystalline materials. All these films, independently of the composition, structure, or production technique, are usually prepared over a substrate material. Thus, the original coating surface properties can affect in a significant grade to the final properties of the film and many researchers focus their efforts on studying these effects and developing new strategies to improve the final quality of films in terms of homogeneity, thickness reduction, thermal and mechanical resistance, and adherence.

Considering all these facts, this chapter is structured in three differentiated sections: (1) Common coating surface materials and main modifications to make the later incorporation of the thin film easier, including chemical or mechanical treatments and incorporation of intermediate layers; (2) Recent advances for preparation of thin films employed as hydrogen-selective membranes; and (3) The most relevant characterization techniques for determining critical properties of these films and developing innovative products.

2.2 Coating Surface and Interface Modifications

Thin film materials for energy applications are usually incorporated onto a support surface to provide specific properties in terms of protection, catalytic activity, or selectivity to a target compound [1]. Only few applications employ directly unsupported thin films with an enough thickness to ensure both thermal and mechanical resistances under operation conditions. An example of these unsupported materials can be found at ENEA laboratories for hydrogen purification [2] and separation of isotopes from nuclear fusion processes [3]. In particular, palladium-based films with thicknesses in the range 50–200 μm are used for these purposes [4, 5].

However, researchers prefer to incorporate a thin film onto a porous substrate in order to decrease the minimum thickness required, saving money but maintaining good properties and mechanical resistance of the system [6, 7]. A wide variety of materials have been proposed as support for the preparation of these composite materials, including Vycor glass [8], metals [9, 10], or ceramics [11, 12]. The selection of an appropriate substrate is crucial, although up to now an ideal solution is not found. Diverse surface characteristics, such as material compatibility, adhesion, mechanical strength, roughness, or porosity need to be considered prior to taking a decision. In fact, metallic supports present an exceptional mechanical resistance that makes the integration in current facilities, usually made in stainless steel, easier. However, they also present a very rough surface with a large pore distribution, which makes the generation of an ultrathin layer without defects really difficult [13]. On the other hand, ceramic supports present a very smooth surface with a narrow pore size distribution that could overcome this problem [14]. Unfortunately, these supports

present a lower mechanical resistance than metallic ones and the thermal expansion coefficient can be significantly different from that of metallic coatings, i.e., palladium or alloys. This fact could represent a relevant inconvenience for an adequate lifespan of the composite membranes [15].

In this context, it is usual to find materials in which the original interface between the support and the thin film has been modified in order to overcome some of these drawbacks, trying to take advantage of other original features [16–18]. Diverse alternatives can be carried out, including chemical or mechanical treatments and incorporation of additional intermediate layers.

2.2.1 Chemical Treatments

The use of chemicals can provoke the modification of original coating surfaces. This technique, very often for modification of polymeric layers, can also be employed for inorganic materials such as metals or ceramics. The treatment is usually known as etching, and it consists of immersing the sample into a corrosive solution, traditionally a strong acid, at controlled temperature to remove part of the material. The effect of the treatment is determined by different factors, emphasizing acid concentration, support composition, temperature, and duration of the process. Mardilovich et al. [19] indicated a double effect of 5 min treating stainless steel surface in hydrochloric acid, increasing the original roughness of the support and providing a preactivated surface for a later deposition. Li et al. [20] used a similar etching treatment at room temperature but with a mixture of hydrochloric and nitric acids. Later, Kim et al. [21] followed this procedure to prepare a composite Pd membrane over a porous nickel support.

In general, it can be affirmed that actually an etching pretreatment on the support is a conventional step in commercial processes for incorporating thin layers on composite materials, independently of using any additional treatment for surface modification [22].

2.2.2 Mechanical Treatments

Other researchers employ physical treatments to modify the original properties of support materials, mainly with the aim of decreasing both pore size and external roughness. Jemaa et al. [23] modified the porous stainless steel surface by high velocity shot peening with ion particles, producing rounded depressions in the surface, stretching it radially and causing plastic flow of surface metal at the instant of contact. As a result, they obtained a smaller average pore size over the modified surface. Jayaraman et al. [24] prepared the supports for a later Pd film incorporation by successive polishing with sandpapers #320, #500, and #800 to smooth the original surface. Mardilovich et al. [19] used a similar mechanical polishing process

with sandpaper over porous stainless steel supports, decreasing both average pore size diameter and roughness. However, a significant porosity loss was evidenced by decreasing the permeation capacity up to 20% of the original one. Li et al. [20] polished the surface of a stainless steel disc using commercial sandpapers with increasing grits step by step, finishing with a #1200 grit sandpaper for about 1 min. Ryi et al. [25] employed similar mechanical polishing treatments over a porous nickel support by using commercial sandpapers followed by wet polishing with alumina powder. The results evidenced a reduction in both roughness and average pore size of the original material, facilitating the later incorporation of a thin selective coating. Pinacci et al. [26] used a similar procedure to reduce the original roughness of stainless steel supports. They modified the materials in a polishing machine with a diamond paste for 8 h, reducing the original roughness from 3.4 to 0.65 μm . Alique [27] presented a complete study of the morphology modification achieved on porous stainless steel supports (PSS) by using commercial silica carbide sandpapers with diverse grits. Figure 2.1 collects the images of the external surface after each treatment. As it can be seen, rougher sandpapers provoke the generation of large defects and grooves due to a plastic deformation of the original material. Moreover, the size of the original small pores is reduced, even disappearing in some samples, while the biggest ones are maintained. In contrast, smoother sandpapers have a finer effect.

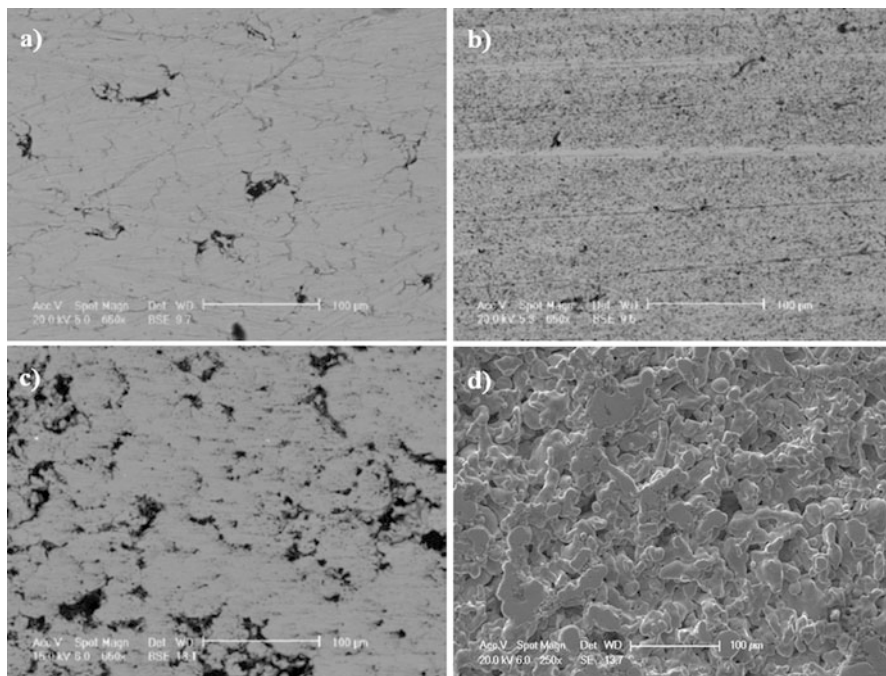


Fig. 2.1 SEM images of PSS supports after polishing with commercial sandpapers: (a) #100, (b) #400, (c) #800, and (d) #1200

The polishing technique not only has been proposed for modifying the surface properties of supports. The reparation of palladium thin films in composite membranes can also be carried out by mechanical treatments, drastically decreasing the remained pinholes on the selective palladium layer [28].

On the contrary, this technique also has detractors due to the negative effect on the permeation capability of the materials. Moreover, several studies also affirm that very smooth surfaces may cause poor adhesion and poor physical strength of the composite membrane, which spoils the long-term stability during temperature and pressure cycling [29]. It is accepted that, in general, the adhesion between a thin film and a support surface depends on the mechanical binding and anchoring effects, thus a minimum roughness of the support it is necessary for a suitable adhesion of the incorporated coatings [30]. Diverse works, as published by Collins and Way [31] and Huang et al. [32], indicate that larger pore sizes and surface roughness of supports results in better adhesion of the thin coating layer. In this manner, it is necessary to achieve a compromise solution between smoothing the original surface and decreasing the average pore size of supports and maintaining minimum values to guarantee a suitable adherence for the incorporated thin film.

2.2.3 Incorporation of Additional Intermediate Layer

The incorporation of additional intermediate layers is one of the most popular alternatives for preparing free-defect thin films on porous supports. Material, thickness, and properties of this interlayer can be adjusted for different purposes, including modification of original morphology, improvement of adhesion capacity, prevention of corrosion, surface pre-activation, or impediment of direct contact between the support and the thin film. Usually, a unique intermediate layer can be employed simultaneously for some of these purposes. The prevention of possible interactions between both support and thin film, mainly in case of metallic materials, is especially relevant for high temperature applications. It is well known that interdiffusion processes appear when metals are maintained in contact at high temperatures, provoking a modification of their original properties [33]. In this manner, many researchers prefer to incorporate an interlayer between the support and the thin selective coating, independently of using any previous additional treatment (i.e., chemical treatment or polishing) to guarantee a suitable behavior of the final composite material. At this point, the selection of the material and thickness of this intermediate layer, as well as the preparation technique, are critical issues to obtain a system with enough mechanical strength and moderate cost [34].

As mentioned in previous sections, ceramic and metallic porous materials are widely used as support for different coatings on the field of environmental and energy applications. Ceramic supports usually are prepared with an asymmetric structure as stacked layers with graduated particle sizes, achieving a very smooth surface with very narrow pore size distribution up to 3 nm [35, 36]. In this case, the use of an intermediate layer is not essential in terms of roughness and pore size

modification and it is really scarce in literature. However, the preparation of asymmetric ceramic supports is relatively costly and the use of macroporous ceramic substrates with symmetric configuration and a very simple intermediate layer could represent an attractive alternative. In this context, Zheng et al. [37] modified a sol–gel method to incorporate an intermediate γ - Al_2O_3 layer over a macroporous α - Al_2O_3 support, showing superiority in smoothening out defects and bumps compared to conventional methods and improving both adhesion between layers and dispersal uniformity of small alumina particles. Over this modified supports, they incorporated a very thin palladium layer of about 4.5 μm without remarkable defects. Hu et al. [38] proposed the modification of a low-cost macroporous Al_2O_3 substrate surface with a conventional 2B pencil composed of graphite and clay, obtaining a free-defect membrane with an external palladium thin film of about 5 μm . Nevertheless, the incorporation of intermediate layers for improving the activation of the ceramic supports prior to incorporating the final thin coating is more usual. One example is the research published by Zhao et al. [39], based on the activation of a ceramic substrate by the sol–gel process of a Pd(II)-modified boehmite sol for the preparation of a composite Pd-membrane with a thickness of about 1 μm . A very particular application is the synthesis of pore-filled type membranes, in which YSZ particles are used to modify the original surface of ceramic supports in a double layer, helping to achieve a good adhesion and uniform coating of the membrane film onto the support and protecting the selective layer [40, 41]. More details about this alternative can be found in the next section, talking of advanced metallic and ceramic composite laminate coatings.

On the other hand, the use of additional intermediate layers is a widespread alternative when metallic supports are used for the incorporation of thin films. As mentioned before, the use of this type of supports for incorporating thin coatings, mainly those composed by other metals such as palladium or alloys, is very attractive due to the excellent mechanical resistance and the facility for integration in conventional equipments [9, 10]. However, the surface properties (high roughness and average pore size) and the migration of components at high temperatures (interdiffusion process), independently of the support grade, represent the main drawbacks that the use of additional intermediate layers tries to resolve [42]. At this point, a wide variety of materials can be found in the literature for obtaining these interlayers and a unique solution is not achieved up to now.

One of the easiest solutions consists of oxidizing the metallic support at high temperatures in air atmosphere in order to generate a mixed Fe_2O_3 - Cr_2O_3 coating as effective interlayer to prevent the interdiffusion process [43]. Ma et al. [44] employed this controlled in situ oxidation method for preparing Pd and Pd/alloy porous stainless steel composite membranes. They found that oxidation temperatures higher than 600 $^\circ\text{C}$ generated oxide layers as effective barriers for avoiding the undesirable intermetallic diffusion. At lower oxidation temperatures, there might still be an oxide layer at the membrane-substrate interface, although it was too thin to be detected. This process was patented as an effective solution for preventing the intermetallic diffusion [45]. Following this patent, Guazzone et al. used oxidized supports in stagnant air at 400–500 $^\circ\text{C}$ to produce an oxide layer as

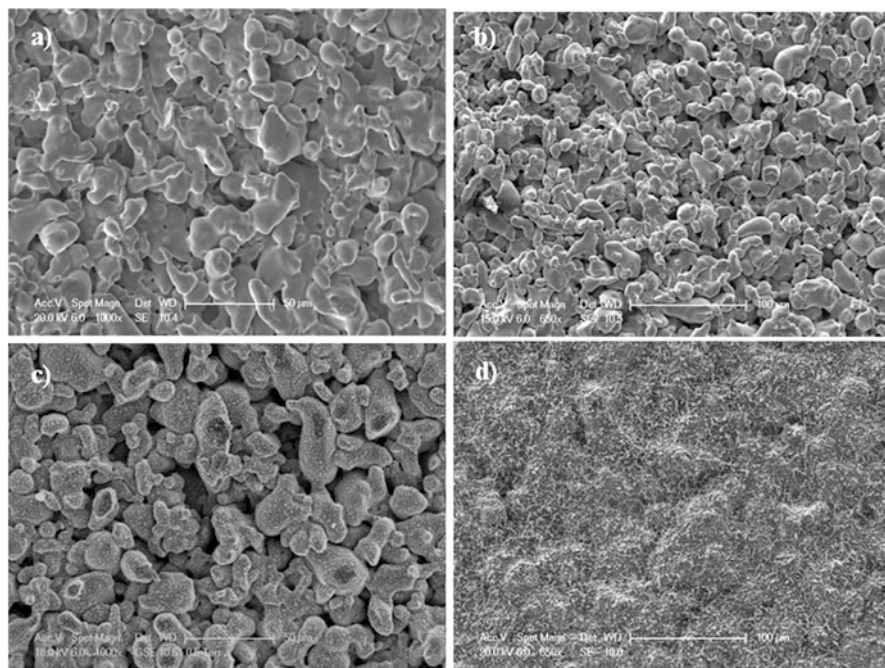


Fig. 2.2 SEM images of oxidized PSS supports at diverse temperatures: (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 700 °C

intermetallic diffusion barrier for analyzing the effects of surface activity, defects and mass transfer on hydrogen permeance, and n -value in composite palladium-porous stainless steel membranes [46]. In the same line, Mateos-Pedrero et al. [47] carried out an oxidation treatment at diverse temperatures (600, 700, and 800 °C with heating ramp rate of 2 °C/min) in air atmosphere for 12 h, detecting a decrease in the permeate flux as the temperature increase. Moreover, they indicated that the achieved surface modifications after the treatments were not enough to significantly decrease the Pd coating thickness in comparison to other alternatives. As an example, Fig. 2.2 shows the results obtained after oxidizing commercial 0.2 μm grade PSS supports at different temperatures. In terms of surface properties (roughness and average external pore size), only slight modifications can be observed after the thermal treatments, except for higher temperatures. For this reason, despite the simplicity of this alternative, many authors choose other kind of materials as intermediate layer for achieving additional surface modifications.

Siliceous materials are the next group of intermediate layers that can be found in the specialized literature. They are considered an interesting alternative due to additional selectivity or catalytic activity in either amorphous or crystalline structures. In fact, microporous silica layers have been applied on porous stainless steel supports to separate H_2 from CO_2 or N_2 without any other additional layer [48] or even combined with palladium in a mixed-matrix structure [49]. As intermediate

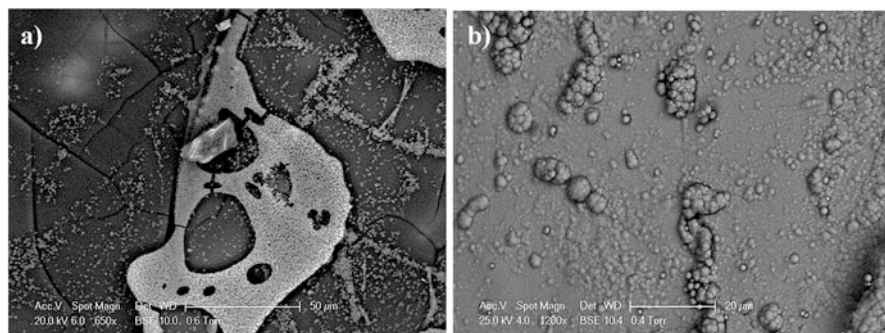


Fig. 2.3 SEM micrograph of silicalite-1 modified PSS support before (a) and after palladium deposition by electroless plating (b) [51]

layer, Nam et al. [50] introduced a thin film of silica by sol-gel method between a selective Pd-Cu layer and a 316L stainless steel substrate to improve the structural stability of the composite material. The membrane, with a 2 μm thickness for the selective layer, exhibited excellent separation performance with hydrogen permeance of $2.5 \cdot 10^{-2} \text{ cm}^3/\text{cm}^2 \cdot \text{cmHg} \cdot \text{s}$ and H_2/N_2 ideal separation factor up to 70,000 at 450 $^\circ\text{C}$. Similar amorphous silica particles have also been employed by Mateos-Pedrero et al. [46], comparing the results obtained in terms of support modification and permeation capacity with other alternatives, such as direct oxidation of the substrate. Calles et al. [51] analyzed the influence of three different siliceous materials used as intermediate layers for composite Pd-PSS membranes: amorphous disordered silica, amorphous ordered silica (HMS), and crystalline silica (silicalite-1). In all cases, both roughness and pore size of the original supports were reduced, allowing to decrease the thickness of the H_2 -selective Pd layer. Among these three diverse materials, silicalite-1 provided the best results with a completely defect-free Pd layer of 5 μm , permeance of $1.423 \cdot 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-0.5}$, and a complete ideal selectivity for hydrogen. Figure 2.3 shows the changes on the morphology of the PSS support after modification with silicalite-1 as intermediate layer and palladium deposition.

One additional step is not only using these silica materials as intermediate layer but applying high temperature resistant silicate gel/ceramic particles for defect repairing of Pd composite membranes as a simply, effective and low-cost method [52].

Considering the relatively good properties of alumina materials as support in terms of roughness and porosity, the use of intermediate layers based on Al_2O_3 have also been proposed by several authors. Thus, Yepes et al. [25] compared the use of $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ oxides as diffusion barriers in composite PSS-Pd hydrogen permeable membranes. Moreover, presented the possibility of using an additional Pd doped thin alumina layer as activated surface. Li et al. [20] employed an alumina coating after other treatments for further smoothening the surface, decreasing the original pore size of the substrate and preventing interdiffusion processes at

elevated temperatures. Broglia et al. [53] incorporated a double layer of γ - Al_2O_3 on a PSS support by dip-coating, followed by drying and calcination, activation of the modified support, and deposition of crack-free Pd layer about 11 μm thick. Chi et al. [54] employed alumina particles of two different sizes to modify the nonuniform pore distribution and the surface roughness of the PSS tubes. Large particles ($\sim 10\ \mu\text{m}$) filled larger pores on the surface and left the smaller ones intact, while small particles ($\sim 1\ \mu\text{m}$) were then used to further decrease the surface roughness, achieving a continuous dense Pd membrane with a minimum thickness of 4.4 μm and good thermal stability. Lee et al. [55] compared the effect of Al_2O_3 and ZrO_2 materials as 200 nm thick intermediate layer for the preparation of a composite PdAu membrane over a porous nickel support. The selective metal incorporation was successful for both intermetallic diffusion barriers although the ZrO_2 interlayer provided 1.5 times higher permeate flux than that achieved by the Al_2O_3 material. Recently, Bottino et al. [56] have determined that the quality of alumina intermediate layers was related to the original surface characteristics of the supports, sol composition (aluminum and additive content), and viscosity of the gel.

Combining silicates and alumina materials is possible to obtain zeolites, with additional benefits on the control of pore structure for molecular sieve applications and catalytic activity. Mabande et al. [57] prepared, with good reproducibility, silicalite-1 and Al-ZSM-5 membranes by combining one-step in situ seeding with one secondary membrane growth step onto PSS substrates. In spite of not using these materials as intermediate layer, they observed comparable hydrogen permeation rates but higher perm-selectivities than obtained for silicalite-1 in case of using the zeolite Al-ZSM-5, despite the lower thickness of the layer. This fact indicates that the use of an adequate zeolite can provide significant advantages for gas separation applications. Bosko et al. [58] presented the synthesis of NaA zeolite by vacuum-assisted secondary growth for modifying the pore size of a PSS substrate and forming a diffusion barrier between the support and a 19 μm thick palladium film. The resulting Pd membrane showed high H_2/N_2 ideal selectivity in the entire working temperature range (400–450 $^\circ\text{C}$). Recently, Dehghani Mobarake et al. [59] have proposed the use of NaX nanozeolites synthesized by microwave heating method for coating the PSS surface to prepare hydrogen-selective Pd-composite membranes. After optimizing diverse synthesis parameters, they have achieved a hydrogen permeation flux of 0.245 $\text{mol}/\text{m}^2\cdot\text{s}$ and ideal selectivity upper than 1,000. Similar works have also been carried out for incorporating zeolites as intermediate layer not only onto metallic supports but also in macroporous ceramic ones [60–62]. The particular properties of zeolites materials additionally can be used for creating a protective coating on the thin selective palladium layer, mainly when these membranes are employed in membrane reactors for hydrogenation or de-hydrogenation processes. Yu et al. [63] proposed the use of a hydroxysodalite, NaA, and Z-21 mixture for this purpose, while Sato et al. [64] employed an FAU-type zeolite and Abate et al. [65] worked with a TS-1 material. In all cases, an increased stability was observed and deactivation effects of the Pd layer by certain compounds were minimized. However, the permeation

properties of the composite material were modified due to the partial coverage of the metal surface with the zeolite material [65].

Many other researchers prefer to employ other types of metal oxides in order to guarantee a similar thermal expansion coefficient between each layer of the composite structure. In this context, the use of ceria (CeO_2), zirconia (ZrO_2), or yttria-stabilized zirconia (YSZ) are the predominant alternatives. Tong et al. [66] obtained a thin Pd layer with 13 μm in thickness on a macroporous stainless steel tube modified with CeO_2 with almost equal hydrogen permeability to the theoretical value for a pure Pd membrane. The stability of the composite was evidenced by the absence of changes after long-term experiments at diverse conditions in morphology, permeation behavior, and hydrogen selectivity. Qiao et al. [67] introduced successfully sol-gel-derived CeO_2 to prevent intermetallic diffusion between a Pd-Cu/PSS at temperatures in the range 300–400 $^\circ\text{C}$ and to enhance the affinity between both layers, support and membrane. Wang et al. [33] incorporated ZrO_2 particles inside the pores of a PSS support to make the preparation of a defect-free palladium film easy, achieving a metal thickness of ca. 10 μm by electroless plating. However, they found that hydrogen permeability for these composite membranes was partly governed by gas diffusion in the pores of intermediate layer. Gao et al. [68] modified PSS disks with a mesoporous palladium impregnated zirconia intermediate layer for preparing thin Pd-Cu membranes near 10 μm thick. This intermediate layer provided seeds for the Pd-Cu film growth and improved the membrane stability avoiding intermetallic diffusion processes and improving the adherence between layers. Lee et al. [55] employed a 200 nm thick ZrO_2 intermediate layer onto a porous nickel support for preparing a Pd-Au selective layer of ca. 3.5 μm , and the results evidenced a better permeation capacity than other membranes prepared with alumina as intermediate layer. Tarditi et al. [69] proposed a vacuum-assisted ZrO_2 incorporation on the top of porous stainless steel disks to enable the formation of defect-free Pd-Au films. In this manner, they obtained a 10 μm thick Pd-Au membrane that exhibits a hydrogen permeation flux of $0.14 \text{ mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$ and ideal selectivity higher than 10,000 at 400 $^\circ\text{C}$ and 100 kPa. Ryi et al. [70] modified planar porous stainless steel supports with ZrO_2 in order to prepare thermally stable palladium composite membranes. Other researchers, such as Huang et al. [29] and Pacheco Tanaka et al. [40], decided to add small amounts of yttria to improve the intrinsic properties of zirconia material, using this yttria-stabilized zirconia (YSZ) as intermediate layer. Following these pioneer works, Zhang et al. [71] incorporated a sol-gel-derived mesoporous YSZ on PSS disks, forming a thin gastight Pd layer with highly stability in the temperature range of 500–600 $^\circ\text{C}$. Sanz et al. [72] prepared a composite material formed by stacked layers of YSZ and palladium onto a stainless steel support and analyzed the permeation properties at different operating conditions for applying a rigorous mathematical model focused on the resistance contribution for each layer. The YSZ intermediate barrier with a thickness of ca. 50 μm was achieved by atmospheric plasma spraying and it let to obtain a completely defect-free 27.7 μm thick Pd film with a permeability of $1.1\cdot 10^{-8} \text{ mol}\cdot\text{s}^{-1}\cdot\text{m}^{-1}\cdot\text{Pa}^{-0.5}$ and complete selectivity to hydrogen. This study was completed by Calles et al. [73] and the permeation

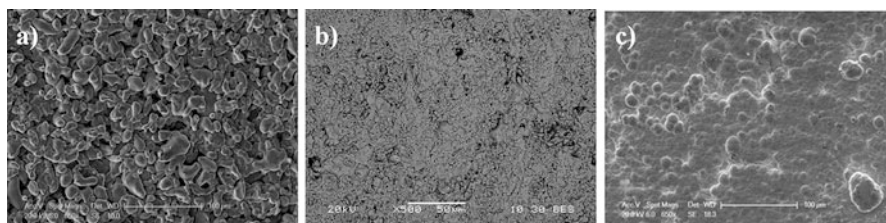


Fig. 2.4 SEM images of: (a) raw PSS support (grade 0.1 μm) (b) YSZ-modified support by Atmospheric Plasma Spraying and (c) composite Pd-YSZ-PSS membrane [73]

behavior of a Pd/YSZ/PSS membrane composite for WGS typical mixtures containing H_2 , N_2 , CO , and CO_2 was published. The membrane was prepared following a similar experimental procedure in both cases, although in the last case YSZ thickness was increased up to 100 μm in order to reduce the selective Pd film up to 13.8 μm . The morphology of the external surface of raw PSS support and its modification after the incorporation of YSZ and Pd layers are collected in Fig. 2.4. As it can be seen, the original PSS surface is practically covered after the incorporation of the YSZ intermediate barrier, decreasing significantly the surface roughness and achieving a very uniform and flat surface with negligible porosity.

Fernandez et al. [9] studied two deposition techniques, atmospheric plasma spraying, and dip-coating of a powder suspension, for preparing ceramic intermediate layers, comparing also the results obtained for zirconia and alumina raw materials. Following these strategies, the most promising membranes required only a Pd-Ag thickness of ca. 4–5 μm with extremely high hydrogen selectivity up to 200,000.

Other alternatives include the use of a wide variety of materials that have demonstrated good effectiveness for preventing the interdiffusion between the Pd-based selective layer and the support. As an example, Nam et al. [9] used a thin layer of TiN obtained by sputtering as diffusion barrier between a Pd-Ni-selective film and stainless steel substrates. Tong et al. [74] prepared a pinhole-free Pd-Ag membrane with a thickness of 3 μm on the surface of a PSS substrate coated with a thin silver layer as a diffusion barrier and aluminum hydroxide gel for filling in the big pores of the support. Ayturk et al. [75] presented a novel bi-metal multilayer (BMML) deposition technique for preparing Pd-Ag composite membranes on PSS supports. The BMML, formed by consecutive deposition of Pd and Ag porous layers with no intermediate surface activation and a final gas tight Pd layer, presented an extremely high efficiency as intermetallic diffusion barrier for over 500 h at temperatures exceeding 500 $^{\circ}\text{C}$. Similar results have been published by Lee et al. [76] with multilayered Pd-Ag introduced in order to prevent Ag segregation to block the intermetallic diffusion from the porous stainless steel and to improve the stability of the membrane. Experimental results showed an extremely efficiency as diffusion barrier and excellent thermal stability for a period of 2,000 h. Chi et al. [77] used a layered double hydroxide (LDH) on a PSS surface to reduce the pore opening of the support and to be a middle layer retarding Pd/Fe

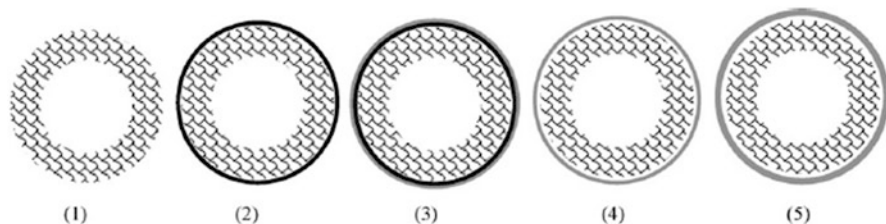


Fig. 2.5 Schematic diagram of cross-sections at different stages in the preparation of defect-free Pd-PSS membranes by using temporary intermediate layer: (1) fresh substrate, (2) polymer layer + substrate, (3) Pd layer + polymer layer + substrate, (4) Pd layer + small gap + substrate, and (5) defect-free Pd layer + small gap + substrate [83]

interdiffusion. With this material, a completely defect-free thin Pd film of around $7.85\ \mu\text{m}$ thick was plated by electroless plating. Pujari et al. [78] proposed the use of nickel as interdiffusion barrier between Pd and PSS, but it was inferred that this route is not fruitful to reduce the critical thickness of dense Pd film without jeopardizing upon the pore densification. Recently, Nayeboossadri et al. [79] have modified the surface pores of PSS substrates by impregnation of varying amounts of tungsten powder that also inhibit the iron interdiffusion between the PSS substrate and the deposited Pd-Cu film at temperature as high as $800\ ^\circ\text{C}$. Nozaki et al. also included hafnium nitride (HfN) as suitable material for non-porous intermediate layer to improve the high temperature stability of Pd-Ta composite membranes for hydrogen separation [80, 81].

One original alternative, only for adjusting the surface properties of supporting materials, but not for avoiding the possible metal interdiffusion, consists of using a temporary intermediate layer. Tong et al. followed this alternative for depositing thin Pd membranes on PSS tubular supports. First, the pores of the substrate are filled in with aluminum hydroxide gel and/or Pd/aluminum hydroxide gel. After that, the selective Pd film is deposited and, finally, the original pores of the support are recovered [82]. Same authors published other similar work in which a polymer was employed as temporary intermediate layer in order to make the incorporation of Pd easy [83]. In Fig. 2.5, a schematic diagram of this interesting process is represented, depicting the composite membrane cross-sections at different stages during the synthesis process.

2.3 Processing of Advanced Metallic and Ceramic Composite Laminate Coatings

In the last few years, a large number of methods have been developed for processing advanced laminate coatings based on metallic and ceramic materials. Pd-based membranes are one of the most representative metallic films for energy and environmental applications due to their really high hydrogen selectivity that

can be applied for purification and CO₂ capture purposes or intensification of hydrogen production processes in membrane reactors [84]. However, palladium availability at reasonable cost for covering all possible industrial uses in the future can be a key factor for real implementation [85]. In this context, the proposed solutions are aimed to develop more efficient preparation processes for obtaining free defects and ultrathin layers or to replace the palladium by an economical ceramic material of similar properties, i.e., cermets [86]. Up to now, the best solution is still under discussion and researchers are divided between different options. In spite of the high cost of palladium, the mechanical properties of the metallic materials and its compatibility with the majority of current devices in the industry, usually made of stainless steel, are propitious and many authors opt for this alternative [85, 87–90]. Considering this fact, this section includes the most relevant advances of common techniques for composite thin film processing, mainly focused on composite Pd-based membranes. At the end, some considerations for preparing other alternative materials have also been included.

2.3.1 Advances in Pd-Based Composite Film Preparation

As previously mentioned, palladium film deposition over a porous support involves a wide variety of techniques, such as Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD), Atomic Layer Deposition (ALD), Molecular Beam Epitaxy (MBE), Electrodeposition (ED), or Electroless Plating (ELP). Among all of them, PVD and ELP alternatives have prevailed in the last years and most of published works in this field include any of them. In these cases, recent advances are directed to reduce the thickness of the palladium layer while maintaining good resistance and mechanical properties [91–93], improve the reproducibility of the preparation method and minimize the number of rejected membranes [94, 95], and combine the unique properties of pure palladium with other metals in alloys to increase the permeability and/or resistance to poisons such as carbon monoxide or sulfur [96–98].

The Physical Vapor Deposition technique (PVD) consists of incorporating metal particles onto a substrate from a vapor phase without any chemical reaction [24]. This metal vapor phase is generated by thermal evaporation at vacuum conditions [99] or, more usually, magnetron sputtering, in which a metal target is bombed with ions of high energy, generating a plasma [100]. The main advantages of this technology are the high control on thickness, being possible to prepare films with only some nanometers, and film composition, especially relevant for the preparation of alloys [101]. This technique is employed by SINTEF for manufacturing ultrathin Pd-alloy membranes of multiple compositions in a patented two-stage technology [102–104]. In a first step, metal films of palladium or palladium alloys are deposited onto a silicon single crystal substrate by magnetron sputtering. Later, the membrane film is removed manually from the silicon substrate, and it is incorporated to an adequate support, usually made of stainless steel. This research

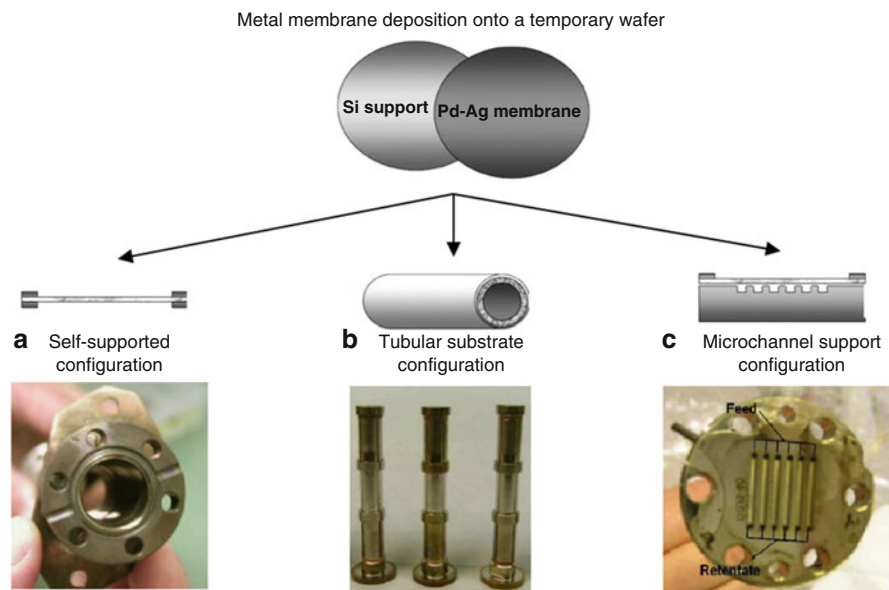


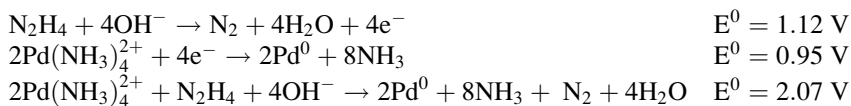
Fig. 2.6 Different configurations for H_2 -selective Pd-based membranes proposed by SINTEF: (a) self-supported membrane fixed in the housing; (b) tubular, mid-section having the active membrane area and (c) microchannel housing membrane. Figure adapted from original published in [104]

group, headed by R. Bredesen, employs the selective film as unsupported membrane or deposited onto conventional supports with tubular geometry or a novel microchannel configuration based on a stainless steel feed channel plate with parallel small channels [104]. In the last case, the thin membrane was placed between the channel housing and a stainless steel plate with apertures corresponding to the channel geometry, obtaining a very compact system with relative high permeation surface. In Fig. 2.6, all these configurations are summarized, including an easy diagram of the support-membrane coupling and a real photo for each particular case.

Anyway, the SINTEF manufacturing technique offers multiple possibilities for investigating tailor-made multicomponent Pd-based alloy membranes with controlled composition, homogeneity, and thickness [105]. In this context, Peter et al. published diverse studies of around $2\ \mu\text{m}$ thick Pd binary and ternary alloys with Ag, Au, Ru, Mo, Ta, Nb, and Y by using this technology [106, 107]. Pd-Au and Pd-Y binary alloys provided the highest H_2 permeability, while in case of preparing ternary alloys is found that the permeability increases with greater fcc lattice constant of the alloy. The addition of small amounts of Ta or Y (1 at.%) over a Pd-Cu increase in H_2 permeability of roughly 10 and 45%, respectively, while the permeability increased in a 65% preparing a ternary Pd-Ag-Cu alloy, compared to the binary Pd-Cu counterpart with equivalent Pd content [106]. They also analyzed the sulfur resistance of these membranes, observing that pure Pd and Pd-Ag films showed instant failures,

while binary Pd-Cu and Pd-Au alloys survived sour atmospheres, although the permeate flux decreased drastically. Moreover, they evidenced that the addition of a third element in some alloys can improve not only the permeability, but also the sulfur tolerance [107]. A similar procedure based on PVD technique is published by Dunbar in order to prepare novel hydrogen-selective thin films [90]. He employed a silicon wafer to incorporate a palladium thin film by thermal evaporation under high vacuum. First, a 20 nm layer of chrome is deposited to act as an adhesion layer of the palladium film, with a thickness of around 1 μm . This method allows the preparation of dense, highly precise and reproducible palladium films with less than 1% variability palladium thickness across the surface. After the metal incorporation, the wafer is treated with a photo-resistant layer and UV light to add a contact mask containing a grid pattern that acts as a mold for a nickel electroplating which builds the mechanical support grid for the palladium film. The complete removal of the mold is critical to a well-functioning membrane. The palladium/nickel composite membrane is released from the silicon starting substrate by dissolving in a hot basic solution and the chrome adhesion layer is selectively etched. The resulting membrane is completely metallic, planar in geometry and contains less than $1.2 \text{ mg}\cdot\text{cm}^{-2}$ palladium metal loading. The membrane exhibited a good performance with hydrogen to helium selectivity of over 5,000:1 and permeance of approximately $3\cdot 10^{-6} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$.

On the other hand, the Electroless Plating technique (ELP) is presented as a very simple method for the synthesis of Pd-based membranes, which does not require any expensive equipment and neither high operational cost due to the absence of electrodes and external sources of electricity [108–112]. This method is based on the deposition of a metal from aqueous solutions onto both conducting and nonconducting surfaces of porous supports with different geometries. Basically, the solution contains a metal-complex that reacts with some reducing agent by a controlled autocatalytic chemical reaction, and it is deposited onto the target surface of the support. For example, most of the Pd-based membranes presented in scientific manuscripts are prepared from $\text{Pd}(\text{NH}_3)_4^{2+}$ and N_2H_4 (hydrazine) as the most common metal-complex and reducing agent, respectively [113, 114]. Next, the main chemical reactions involved in the process, including the hydrazine oxidation, the metal reduction, and the global reaction, are described as:



In general, prior to carrying out the metal incorporation, it is necessary to activate the surface of the support in order to decrease the activation time for the film generation and improve the homogeneity of the coating [115]. Traditionally, the activation process of different types of support has been carried out by using successive immersions in acidic solutions of tin and palladium in the so-called sensibilization-activation method [116]. However, recent studies have analyzed the influence of Sn residues on the stability of composite palladium membranes. It was

found that the higher concentration of tin solution, as well as the number of sensibilization-activation cycles, enlarged the Sn residue amount and led to a lower initial selectivity but a better membrane stability [117]. Considering the possible negative effects of tin residues, some authors have presented alternative methods for generating the first Pd nuclei avoiding the use of tin solutions. In this context, as it is already described in previous sections, some authors used the incorporation of an intermediate layer between the porous support and the selective coating to include homogeneously distributed nuclei [68, 71, 75–77]. Touyeras et al. [118] carried out the activation step in an ultrasonic bath to increase the nuclei deposition rate and avoid the generation of conglomerates on the support surface. Sanz et al. [95, 119] employed a direct reduction method of a diluted palladium solution to activate the surface of porous stainless steel supports and Seshimo et al. [120] investigated the use of catalyzed anodic alumina surfaces to facilitate the Pd electroless plating.

However, in spite of the substrate selection and a correct surface activation are key factors on the quality of the final coating, most researchers concentrate their efforts on reducing the metal thickness and improving the membrane properties by modifying the conventional electroless plating method. Thus, Uemiya et al. [121] proposed to increase the metal incorporation rate by immersing previously the porous substrate in a hydrazine solution. Yeung et al. [122], Souleimanova et al. [123] and Li et al. [124] combined the ELP technique with osmosis to facilitate the incorporation of the metal in the pore areas. Zhao et al. [39] and Zhang et al. [125] employed a vacuum-assisted ELP with similar purposes, obtaining Pd composite membranes with finer and more uniform microstructure. On the other hand, some authors are focused on modifying the composition of solutions employed in the ELP process in order to improve the properties of the deposited film. Most of them propose the use of free-EDTA baths to avoid the presence of carbon deposits on the selective metal film that can react at particular conditions for generating CO₂ and, consequently, defects in the coating [126–128]. Finally, the influence that supports rotation during the ELP process has also been studied, considering this alternative simple and easily scalable for mass production. Chi et al. [129] determined that the rate of Pd deposition increased as the support rotation rate does. Compared with conventional ELP in static, the proposed modification using support rotation yielded Pd membranes with more uniform and smooth surface morphology, which substantially enhanced the membrane stability. These membranes exhibited a permeance of $3.0 \cdot 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-0.5}$ with ideal hydrogen separation factor upper than 400 with only 5 μm thick.

In addition to all developments above collected, it is important to emphasize that many membranes are usually rejected during their manufacturing process due to the presence of defects, increasing the overall cost of the ELP process that makes the industrial scale-up difficult. In this mean, it is crucial to improve the current procedures and develop new routes for the generation of low-cost thin films by ELP with high reproducibility. Recently, some authors have developed novel alternatives to repair defects produced during the fabrication of composite Pd-based membranes. From this angle, Li et al. [124] reported the combination of

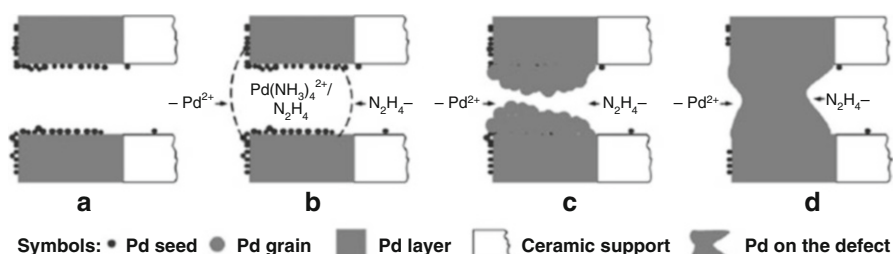


Fig. 2.7 Stages of defect sealing during the Pd pore-plating [94]

conventional ELP and osmosis for repairing defects in Pd/ α -Al₂O₃ composite membranes. They affirm the complete disappearance of defects, evidenced by a significant increase of hydrogen perm-selectivity without any reduction of the permeation flux or increase in the selective film thickness. Following this pioneer work, Zeng et al. [94] presented the so-called point plating as an attractive alternative for repairing small defects and cracks in palladium membranes. The point plating method is based on the conventional chemical reactions of electroless plating, but feeding the palladium salt and the reducing agent from opposite sides of the composite membrane. In this manner, the selective deposition of palladium is forced to be place just over the palladium layer defect. Figure 2.7 shows a scheme of the progressive defect sealing following the proposed technique:

Based on both pioneer methods, the Chemical and Environmental Engineering Research Group of the University Rey Juan Carlos has developed a new route to prepare very reproducible defect-free palladium composite membranes by incorporation of palladium directly over tubular commercial porous stainless steel supports by modified electroless plating [43, 95, 119]. This new method is called Electroless Pore-Plating (ELP-PP) and consists on feeding the solution that contains the Pd source and the reducing agent (hydrazine) from opposite sides of the support from the first stages of the membrane conformation. In this manner, the chemical reaction between Pd²⁺ ions and the reducing agent is initiated in the internal porosity of the support, in a similar way to the method proposed by Zeng et al. [94] for defect sealing. However, there is no any previous palladium layer in this case and the palladium incorporation is performed directly over both commercial and modified PSS supports. The main advantage of this method is that a minimum palladium thickness for a complete coating is guaranteed due to the palladium incorporation turns difficult the encounter of reactants until all pores become completely filled and the process ends. Figure 2.8 reproduces simple schemes for both conventional ELP and the novel ELP-PP in order to evidence the benefits of the last one. At this point, it is important to emphasize the noticeable reduction of preparation costs for these composite membranes.

The membranes obtained by the novel ELP-PP method evidenced that palladium was not only incorporated on the pore areas, and an external film was generated on both commercial and modified PSS supports. The authors explain this fact is produced by the presence of a wide variety of pore diameters in the PSS supports.

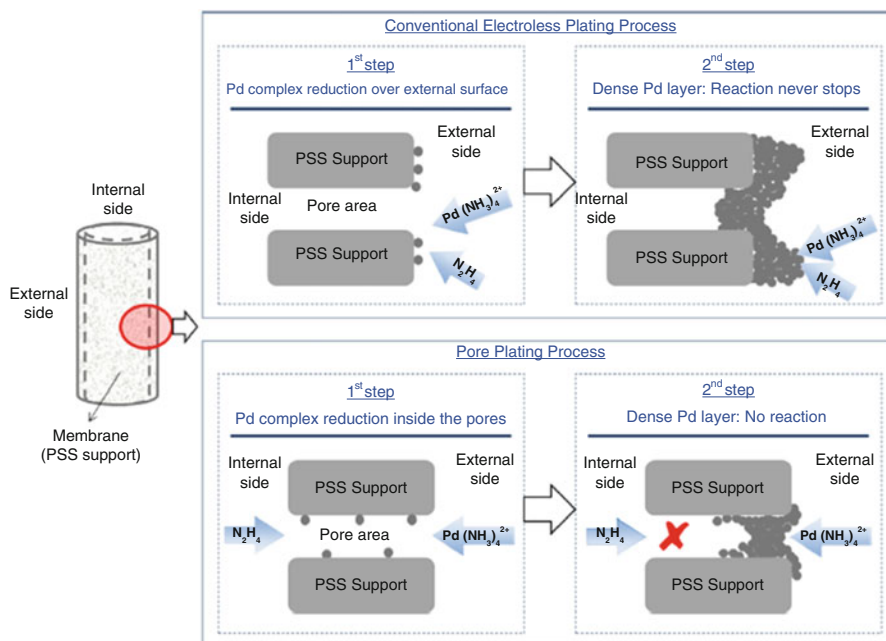
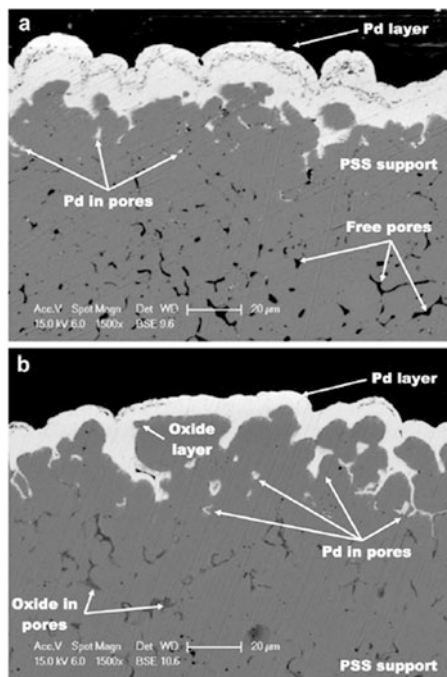


Fig. 2.8 Comparison of conventional Electroless Plating and novel Pore-Plating techniques [95]

The smallest pores can be fully closed by palladium incorporation in a relative short time, but the hydrazine can diffuse from the internal to the external side of the support through the biggest ones, partially covered, where reacts with the Pd solution and generates an external layer. Thus, support characteristics, concentration of solutions, and the ratio membrane length/solution volume during the process define the palladium distribution in the composite membrane. As an example, the use of calcined supports for reducing the original average pore diameter of pores provokes a significant reduction in the final thickness for the composite Pd membranes from 20 to 11 μm (estimated value from gravimetric analysis). In both cases, the real external thickness is around 2–6 μm lower than the previous estimated value due to the partially infiltration in the pores close to the external surface of the support. The palladium distribution for each membrane is showed in cross-sectional SEM images reproduced in Fig. 2.9. This research group also demonstrates the quality and high stability of the membranes prepared following this method through both permeation experiments and tests in a real membrane reactor for the water gas shift (WGS) process [43, 95, 119]. In all cases, the membranes maintained a good integrity, complete hydrogen selectivity and permeances in the range $1\text{--}6 \cdot 10^{-4} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-0.5}$.

Recently, the ELP-PP technique is also applied onto ceramic substrates, evidencing the possibility to generate an ultrathin selective layer by this technique over a support with vary small pores and a narrow pore size distribution, although the presence of palladium in both internal pores and external surface is still presented [130].

Fig. 2.9 SEM micrographs depicting cross-sections of: (a) PSS-Pd and (b) PSS-OXI-Pd composite membranes [95]



Other interesting alternative is proposed by Pacheco Tanaka et al. [40, 131, 132] that consists on the preparation of pore-filled membranes by the incorporation of the selective metal between two ceramic layers in a sandwich-type structure. Following this procedure, the palladium nanoparticles are deposited through vacuum-assisted electroless plating, taking up the free spaces leaving between the ceramic particles of a first interlayer, which is covered later by a new ceramic layer. In this way, the advanced composite membranes are able to work below the critical temperature and maintain a high stability, instead of conventional membranes based on an external coating, where fatal damages usually occur. Recently, a clear scheme of the conformation process following this procedure has been published by Arratibel et al. [41], and it has been reproduced here with permission in Fig. 2.10.

Independently of using a conventional or a improved electroless plating technique, most researchers combine the palladium with other metals for improving permeate flux, mechanical stability, and poison tolerance of the composite membrane in a similar way that works previously presented for PVD methods. In this context, the research group headed by J.D. Way has so many years of experience preparing diverse binary and ternary alloys with copper [133–136], gold [16, 96, 137–140], silver [16, 138, 141], and ruthenium [142]. Braun et al. [143] prepared a ternary Pd-Ag-Au layer over a porous stainless steel support by sequential electroless deposition and studied the morphology and microstructure of the membrane before and after permeation tests in the presence of sulfur. Miller et al. [144] collected the physics and chemistry of H_2 transport through dense Pd-alloy layers in

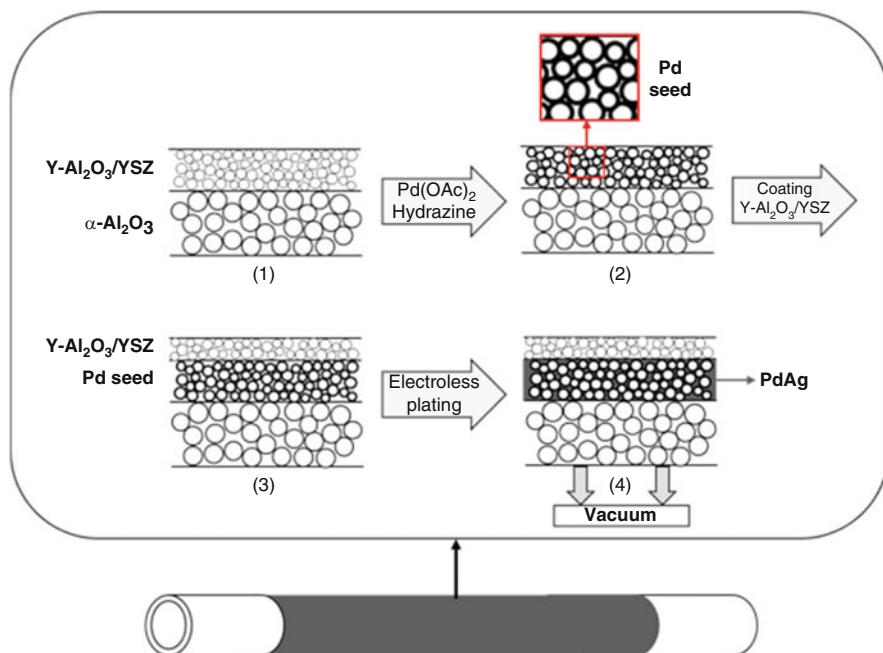


Fig. 2.10 Schematic description of the preparation of Pd pore-filled membranes [41]

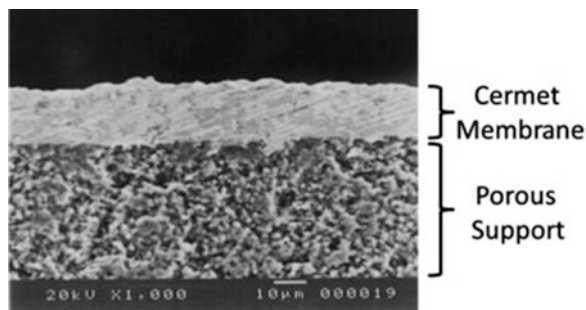
a book chapter, as well as the permeation behavior modification in the presence of pollutants typically present in stream from fossil energy. The list of published works is very long, but the main objective in all cases is to increase the permeance of the membrane in unfavorable operational conditions.

As a general conclusion, it can be pointed that a wide variety of strategies are being followed to develop new Pd-based composite coatings, achieving free-defect thin films with good reproducibility and resistance at reasonable cost. In fact, after the last advances, the cost of the selective coating is within the average cost of the support materials, in spite of being composed by noble metals.

2.3.2 Alternative Materials to Metallic Thin Films

In order to avoid the use of large amounts of noble metals for preparing hydrogen-selective films, some researchers have proposed the fabrication of membranes based on alternative materials. In this context, non-Pd BCC alloys and proton conducting membranes stand out as attractive option for reducing the cost of materials while a significant hydrogen permeability is maintained [145]. Dolan presented a review of diverse body-centered-cubic (BCC) alloys comprising Group IV and V metals as suitable materials for high temperature hydrogen separation

Fig. 2.11 Cross-sectional SEM image of a supported cermet membrane [86]



applications, overcoming the traditional embrittlement problem and enhancing the permeation capability [146]. On the other hand, Tao et al. [147] recently published a complete overview of last developments with dense proton-electron conducting ceramic materials and their associated membranes. These materials have been classified into categories by typical composition formulation. As a conclusion, these researchers showed that proton-electron conducting ceramic membranes are not yet ready for industrial requirements. In order to overcome the current limitations of these materials, the authors proposed some recommendations to address the future necessary challenges, mainly including the analysis of new formulation to enhance the conductivity and mechanical properties and developing of mathematical models for better understanding the behavior of these materials. The use of cermet materials combines the properties of ceramic with metallic components in a composite structure with enhanced permeance. In general, for the preparation of these materials, both ceramic and metallic powders are mechanically mixed, pressed and sintered at high temperature (upper than 1,200 °C). After that, for the film preparation, the cermet powders are dispersed in an alcohol solution and mixer with other compounds as binder and plasticizer to obtain a malleable paste that is incorporated onto a porous substrate by a painting method. Balachandran et al. [86, 148, 149] employed this type of materials as a thin film with thicknesses in the range of 22–200 μm for hydrogen separation processes with acceptable permeance and high selectivity. Figure 2.11 shows a cross-sectional micrograph of a typical cermet membrane prepared by this research group by using a porous ceramic support.

2.4 Characterization Techniques

After processing any coating or thin film material for energy and environmental applications, an exhaustive and complete characterization is a critical issue necessary to ensure the correct operational behavior for the complete lifespan of membranes. A large variety of techniques can be used for this purpose, being usually classified as morphological analyses, determination of mechanical properties, and

permeation tests. The first group includes all techniques aimed to determine the main structural properties of the materials, i.e., continuity, porosity, roughness, thickness, composition, or crystallinity. The second one is focused on the analysis of critical mechanical properties, such as hardness or adherence of coatings. All these properties can be used for predicting the future behavior of the membrane and define the most appropriate applications for each material. However, it is necessary to demonstrate the capability of the material through permeation tests at diverse conditions as real as possible in both laboratory and pilot-plant scales.

This section tries to gather the most common characterization techniques, describing the basic principles and usual applications for each one.

2.4.1 Optical Microscopy and Profilometry

One of the oldest techniques to analyze the morphology of coatings and thin films materials is the optical microscopy (OM), which is usually capable of achieving a resolution up to 300 nm, around 200 times upper the human eye limitation. In the last years, this technique has been developed to offer better possibilities. Particularly, confocal microscopy offers several advantages over conventional optical microscopy, including controllable depth of field, the elimination of image degrading out-of-focus information, and the ability to collect serial optical sections from thick specimens. The key to the confocal approach is the use of spatial filtering to eliminate out-of-focus light or flare in specimens that are thicker than the plane of focus. The relatively low cost of optical microscopies has been favored their diffusion and many researchers use this technique to analyze the morphology of thin films. Usually, the images obtained from optical microscopy are used to observe changes or damages in the coatings after thermal treatments or mechanical stresses, as well as for detecting cracks and pinholes. In Fig. 2.12, a Pd membrane surface is analyzed by this technique in order to observe the progressive defect sealing by the point-plating method developed by Zeng et al. [94].

Associated to the optical microscopy, it is possible to find a profilometer integrated in a computerized system for roughness determination and recreating the real surface in a 3D image. In general, these systems scan the surface of the sample and record all areas in focus, repeating the process for different values of the Z axis. An example of the surface recreation for two commercial PSS supports with diverse characteristics (porosity grade 0.1 and 0.2 μm) can be seen in Fig. 2.13.

2.4.2 Scanning Electron Microscopy

The scanning electron microscopy (SEM) is a very useful tool for morphology and structural characterization of solid film surfaces with high resolution at micron scale. Surfaces with dimensions ranged from 1 cm to 5 μm can be usually analyzed

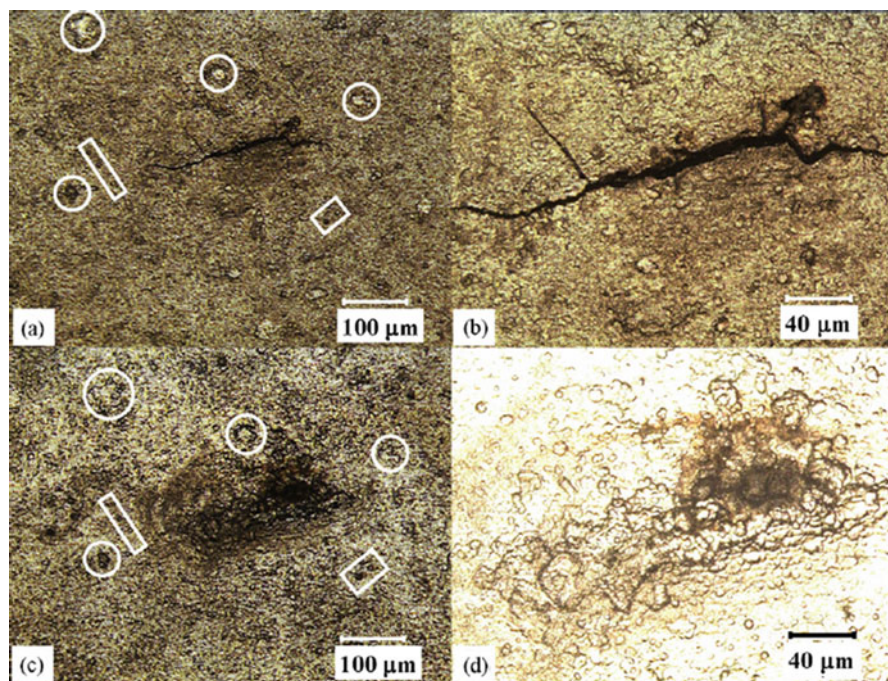


Fig. 2.12 Surface images of a Pd membrane surface by optical microscopy at different magnification: (a, b) crack detection and (c, d) repaired area after point plating [94]

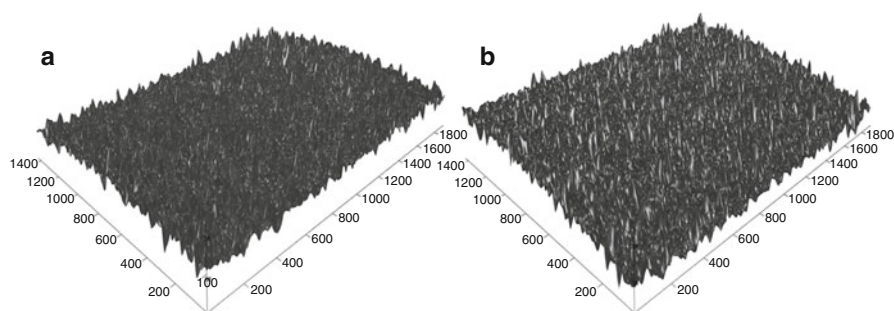


Fig. 2.13 Surface 3D reconstruction of commercial PSS supports with porosity grade: (a) 0.1 μm and (b) 0.2 μm

varying the magnification. This technique is based on the scanning of a target surface by focusing a beam of high energy electrons to generate multiple signals from electron-sample interactions such as secondary (SE), backscattered (BSE), or diffracted backscattered electrons (EBSD). SE and BSE are the most common signals used for imaging thin films and coatings of composite membranes. The amount of detected SE is function to the topography of the sample, decreasing

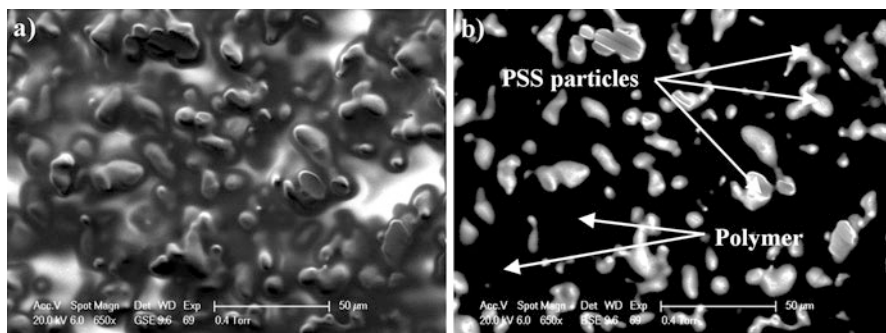


Fig. 2.14 Conventional SEM images of a membrane surface obtained by: (a) SE and (b) BSE

the signal for deepest areas and increasing for raised ones. On the other hand, the amount of BSE can be directly related to the composition of the sample, obtaining bright areas when heavy atoms are dominant and a dark color for areas where light atoms, i.e., carbon, are the larger part.

Figure 2.14 shows the surface of a porous stainless steel support modified by the incorporation of a polymer material with both detectors, SE and BSE. The external morphology of the sample can be clearly analyzed from the SE mode image (Fig. 2.14a), obtaining an apparent good continuity, absence of pores, and a certain roughness. On contrast, the image obtained from BSE evidences the presence of different tones due to composition changes on the sample (Fig. 2.14b). In this manner, the brightest areas correspond to the highest stainless steel particles, not affected by the incorporation of the polymer, which appears dark due to the low molecular weight of the carbon mainly present in the structure.

At this point, it is important to emphasize that it is possible to complete the characterization obtained from these SEM images with help of diverse commercial processing tools, such as Scanning Probe Image Processor[®] (SPIP[®]) or Digital Micrograph[™] [51, 72, 73]. Basically, they allow determining quantitatively relevant parameters of the studied surface. In fact, SPIP[®] software calculates an apparent external roughness from the SE mode image and offers the possibility to reconstruct a 3D image in a similar way to the previously described optical profilometers. On the contrary, Digital Micrograph[™] software uses the micrograph obtained from BSE mode and segments the images for distinguishing the solid areas in some grey scale from the dark pores. In this manner, considering the total size of the analyzed area, the external porosity can be determined.

Other conventional application of SEM pictures is to determine the thickness of intermediate layers and selective coatings by visualizing the sample cross-section. As an example, Fig. 2.15 shows an SEM photograph of a composite membrane cross-section formed by stacked layers of stainless steel (main support), silicalite-1 (intermediate layer), and palladium (selective layer for hydrogen permeation).

Moreover, it is also possible to analyze the generation of X-rays produced by inelastic collisions of the incident beam with other electrons of atoms present in the

Fig. 2.15 Micrograph of a composite membrane cross-section with thickness measurements

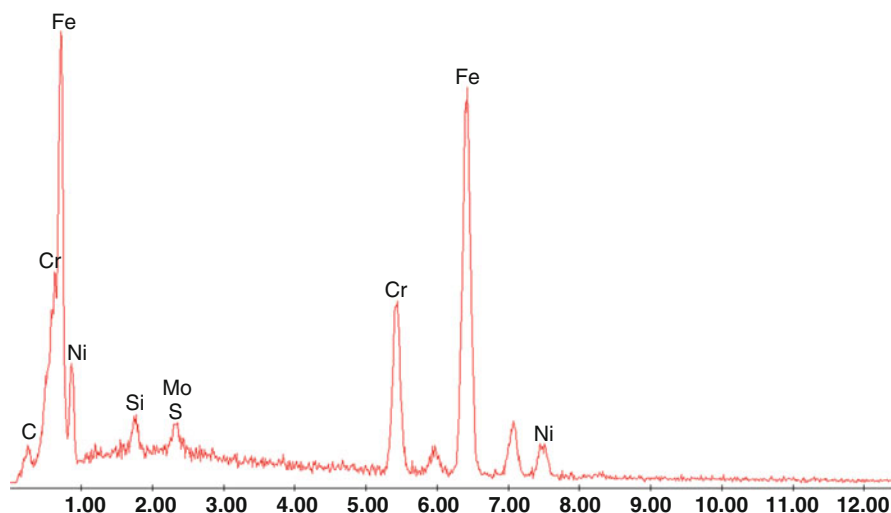
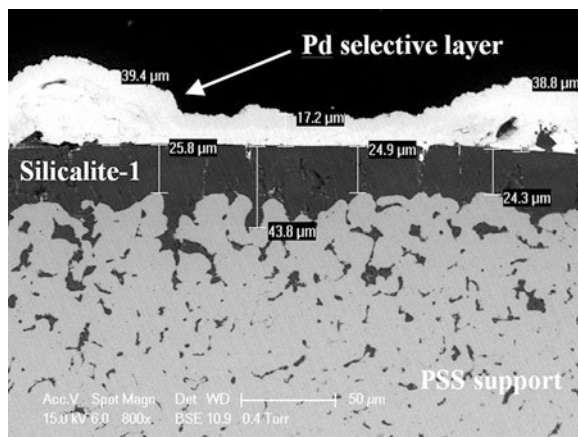


Fig. 2.16 EDX spectra for a porous stainless steel membrane

sample by an EDX detector. Currently, most scanning electron microscopes are equipped with this accessory. The excited electrons of the sample by the incident beam return to lower energy states yielding X-rays of fixed wavelength characteristic for each element. In general, for the analysis of inorganic materials, SEM analysis is considered to be nondestructive and X-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly. Figure 2.16 shows the X-ray spectra obtained for a 316 L stainless steel material, being possible to distinguish iron, chromium, nickel, silica, molybdenum, and carbon as main components.

One popular application for the in situ composition analysis inside an SEM is the characterization of alloys. Combining both surface visualization and EDX analyses,

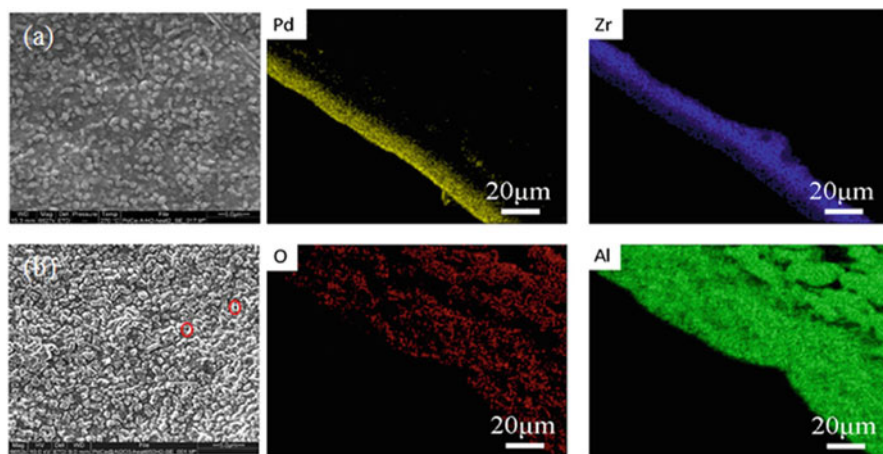


Fig. 2.17 SEM images of a composite Pd membrane at diverse conditions: (a) after heating to 250 °C under H₂ gas (1 Torr, for 20 min) and (b) heated to 650 °C in succession (pinholes are highlighted in red cycles). (c) Element mapping of Pd, Zr, Al, and O from the cross-section of sample [150]

it is possible to study the distribution of each metal that form the alloy. This is very useful for ensuring the preparation of homogeneous alloys and analyzing the intermetallic diffusion process when diverse metal layers are in contact for long time at high temperatures. As an example, Zhu et al. [150] carried out element mappings of a composite membrane formed by stacked layers of ZrO₂ (15 μm thick) and Pd (4 μm thick) onto a ceramic support in order to study both micro-structure and composition of the composite system under diverse gas-thermal treatments. Figure 2.17 contains the SEM surface images of the membrane at two different thermal conditions, as well as the elemental mapping obtained from EDX analyses for each case.

2.4.3 Auger Electron Spectroscopy

The auger electron spectroscopy (AES) is a widely used technique to investigate the composition of surfaces, and it is certainly similar to the previously described EDX technique. The AES technique is based also on the ionization of a core atomic state by an incident electron beam. In general, the excited atom can relax through two different competitive effects: emission of photons (X-ray) or electrons (Auger effect). The first case is favored in case of heavy elements are predominant in the thin film, while the Auger effect appears clearly for light elements. Thus, characterization by EDX is usually the dominant technique for determination of composition in most inorganic films, while AES is less extended and only few works employ this technique for the analysis of impurities on the surface of inorganic thin

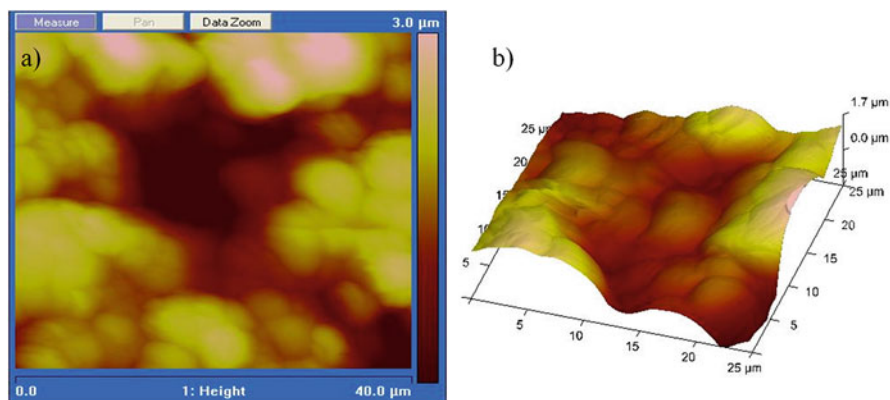


Fig. 2.18 (a) Image of a Pd-composite membrane directly obtained by AFM and (b) 3D recreation

films and coatings. For instance, Antoniazzi et al. [151] studied the effect of carbon surface impurities on the hydrogen permeation rates of a dense palladium membrane by in situ monitoring of the membrane and Auger analysis.

2.4.4 Atomic Force Microscopy

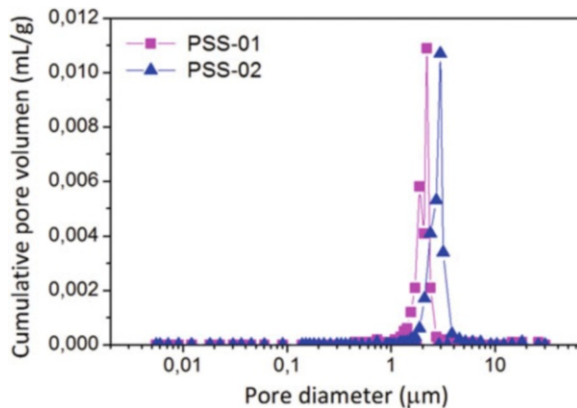
This type of microscopy employs a mechanic-optical instrument able to detect forces in the range of piconewtons. The microscope is usually equipped with a sharp tip with conic or pyramidal geometry that scans the sample. The tip is connected to a cantilever spring to let free movements onto the surface topography. Each variation of the tip position is detected by a laser diode, and the information is used to recreate accurately the analyzed surface. In this manner, the atomic force microscopy can be used for studying the morphology of diverse materials with even higher resolution of traditional scanning electron microscopes, achieving extremely high magnifications up to 1,000,000x.

Figure 2.18 shows the image obtained directly with an AFM for a Pd-composite membrane and the three-dimensional recreation of the surface in order to visualize clearly the morphology and roughness of the sample.

2.4.5 Mercury Porosimetry

The mercury porosimetry is an indirect technique for the characterization of the porous structure of a sample, mainly the pore volume, porosity, average pore size, and tortuosity of the pores. It is based on the capillarity properties of pore internal

Fig. 2.19 Pore size distribution of porous stainless steel filters determined by mercury porosimetry



channels and the low capacity of mercury to wet the surface of solids. In this manner, it is necessary to apply some pressure to introduce the mercury inside the pores so much as the pore is narrower. The conventional procedure consists of immersing the sample in a mercury bath and progressively increases the pressure. For each value of pressure, the equipment determines the volume of the metal that penetrates into the pores. This volume provides information about the porosity of the sample, and the pressure can be related to the pore size. Typically, pore sizes ranged from $3.0 \cdot 10^{-3}$ to $1.0 \cdot 10^3$ can be measured. Figure 2.19 shows a typical pore size distribution of two different porous stainless steel tubes with grade 0.1 and $0.2 \mu\text{m}$ obtained by mercury porosimetry.

2.4.6 X-Ray Diffraction

X-ray diffraction (XRD) is an analytic technique employed for identifying crystalline structures of solid samples, being possible to distinguish diverse allotropic or isomorphic phases. A crystalline material can be considered a periodic and ordered group of atoms. When the material is reached by an electromagnetic radiation with wavelength near to the interatomic distance, constructive interactions in particular directions appear. In this way, the diffracted beam will rely on the type of atoms in the sample and their geometric positions, generating a unique diffraction spectrum for each crystalline material, like a finger print.

The analysis of a sample by this technique is based on the Bragg's law that connects the wavelength of the incident X-ray (λ), the distance between crystalline planes (d), and the angle between both (θ).

$$n \cdot \lambda = 2 \cdot d \cdot \sin(\theta)$$

When this equation is reached, the reflected rays by the crystal generate constructive interferences. Otherwise, destructive interferences are produced and no signal can be observed. In this manner, a typical XRD pattern represents the angular positions of each signal, and the identification of each crystalline phase is carried out by comparison with other patterns. The intensity for each signal can be related with the amount of that crystalline phase in the sample.

Traditionally, the use of XRD analyses is very attractive for studying the synthesis or ordered materials or following the alloying processes for the preparation of advanced materials. As an example of this technique application, Fig. 2.20 presents high temperature X-ray diffraction measurements carried out by Pati et al. [152] for pure palladium and palladium-rich alloys. The lattice parameters, coefficient of thermal expansion, and X-ray Debye temperature of these materials were calculated as a function of temperature from the XRD data.

2.4.7 X-Ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is also one of the most widely used techniques for the surface analysis of thin films and coatings. This characterization technique can be applied to a wide variety of materials and provides valuable quantitative information about both elemental composition and chemical state of the species. The technique is based on the irradiation of a surface with an X-ray beam at high vacuum and measurement of both kinetic energy and number of electrons that escape from the top of the sample. The obtained results usually are related to an average depth of around 5–10 nm. Combining these measurements with some milling treatment, it is also possible to analyze accurately both elemental identity and chemical state of the sample at entire thin film thickness. In general, the XPS results of a thin film structures are very useful for many industrial and research applications where the composition plays a critical role in performance.

As an example, Fig. 2.21 shows the XPS spectra obtained for two different Pd coatings onto an alumina substrate presented by Elam et al. [153]. A typical signal of pure palladium metal can be distinguished at a binding energy of around 335 eV for the sample with 51 Å thick (pick identified as Pd3d). The lightly increase of the energy for this signal in the thinner sample (13 Å thick) indicate oxidation of the palladium, suggesting that much of the Pd is bound to oxygen atoms of the alumina support.

Other examples of using XPS analysis for characterization of thin films can be found in the works presented by Leiro et al. [154] for the analysis of surface segregation and core-level shift of a Pd-Rh alloy film, Tang et al. [155], focused on the study of composition and corrosion resistance of palladium film on 316 L stainless steel by brush plating, and Skoryna et al. [156] for valence band studies of nanocrystalline Pd-Zr alloy thin films.

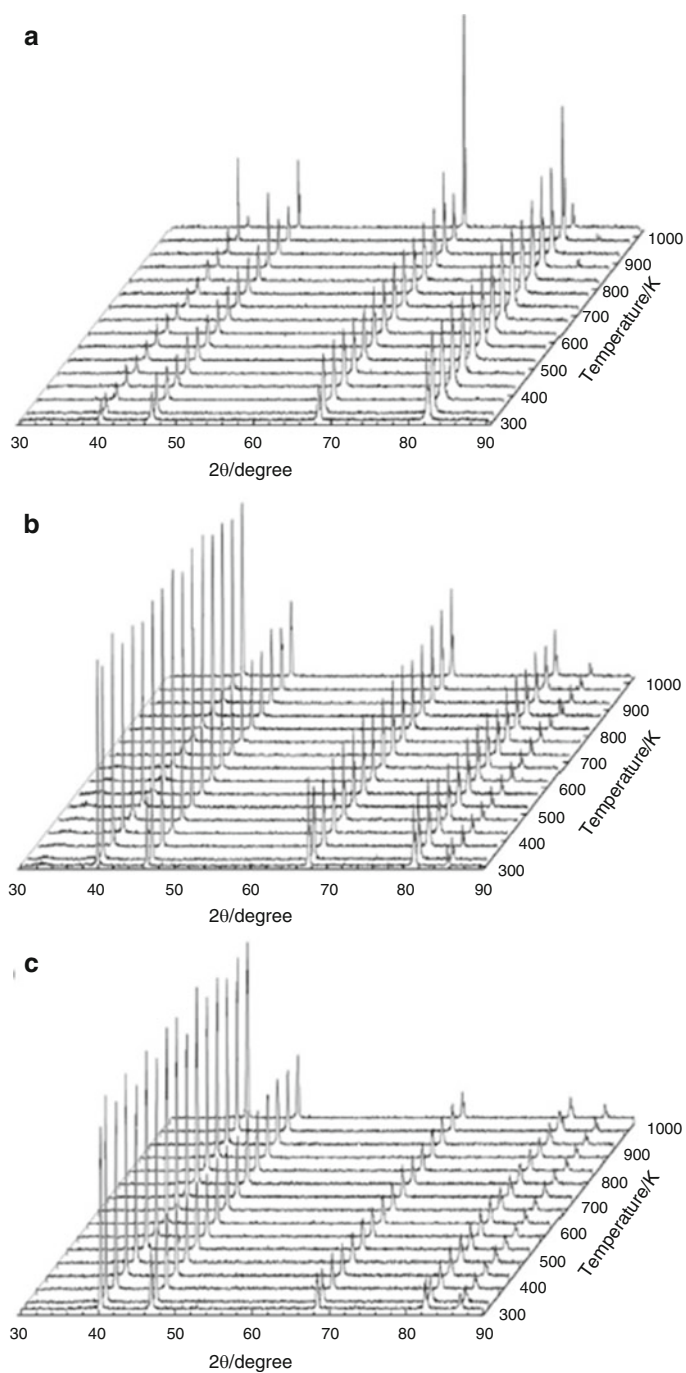


Fig. 2.20 High temperature XRD patterns of: (a) Pd, (b) $\text{Pd}_{77}\text{Ag}_{23}$, and (c) $\text{Pd}_{77}\text{Ag}_{10}\text{Cu}_{13}$ [152]

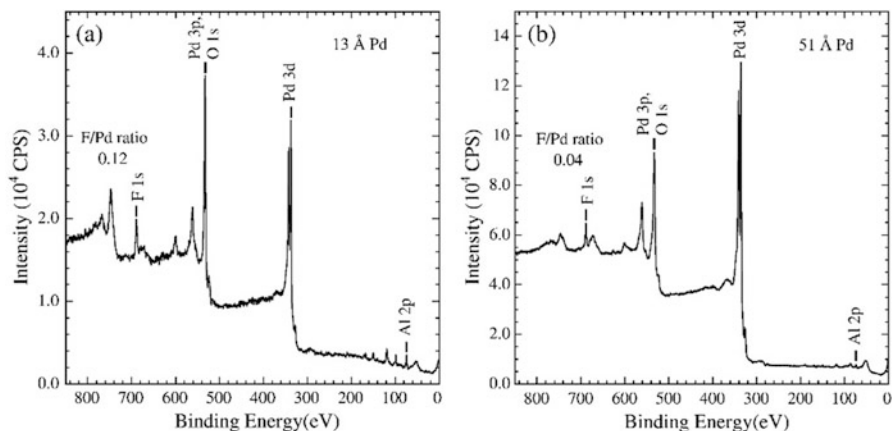


Fig. 2.21 XPS spectra for two different Pd coatings on Al_2O_3 . Film thickness: (a) 13 and (b) 51 Å [153]

2.4.8 Gravimetric Analysis

The gravimetric analysis is a quantitative method for determining the weight variation of a sample after certain processes. This simple method is very common for the thickness estimation of selective film coatings, considering the geometry of the surface, the composition of the film, the density of each component, and a homogeneous deposition process. In this manner, an average thickness value for the coating is usually obtained in good agreement with the real value, determined necessary by SEM. Main deviations are usually attributed to a heterogeneous incorporation or the partial penetration of the coating into the porous structure of the support [95].

2.4.9 Mechanical Resistance and Adherence

Mechanical properties of coatings and thin films are critical issues for ensuring a suitable behavior of composite materials in real applications. In this context, the main concerns that it is necessary to take into account are adherence to the substrate, stresses present in the composite material, thermal resistance, hardness and wear resistance [157]. It is clear that a composite membrane formed by stacked layers of a porous substrate and a thin selective film is exposed to a wide variety of factors that can compromise its integrity. Firstly, the operation mode in terms of permeate flux direction strongly affects to the resistance of the films. Stresses and delamination can be produced when the permeate flows from one side of the support to the other side where the selective film is deposited [158]. Thermal resistance is one of the most important aspects that it is necessary to take into

account, especially in case of using cycles of temperatures during the membrane operation, i.e., for a noncontinuous operation and adsorbent or catalyst regeneration varying the temperature in membrane reactor applications [54, 159]. For Pd-based membranes, hydrogen embrittlement can also be considered if temperature drops under 297 °C [160–162]. Moreover, the intrinsic thermal expansion coefficient of each material that compose the composite membrane also represents a critical parameter that it is necessary to analyze, mainly in case of using a multilayer structure, i.e., including an intermediate layer between the support and the selective thin film or a final protective coating [163]. Adherence between substrate and coatings is other fundamental parameter from the first preparation stages. Surface properties of substrate, composition, and deposition techniques are the main responsible of the film adherence. As mentioned in previous sections, smooth surfaces of supports make the adherence of the thin film weak, while a certain roughness improves the anchoring between both layers, in spite of hindering the generation of a free-defect low thickness [29, 30]. Finally, hardness and wear resistance of the incorporated thin film is also essential, especially in case of working in fluidized-bed membrane reactors, in which catalyst particles are in constant movement, hitting with the thin film [164, 165].

Although electrical properties are usually showed in specialized literature as a separated category from mechanical properties, they can also be relevant for some particular applications in case of using metal thin films. As an example, Tosti et al. [166] studied the electrical resistivity of a Pd-Ag permeator tube under different hydrogenation conditions for heating the membrane system. From this perspective, the electrical resistance of the membrane film when a voltage difference is applied provokes an ohmic effect and the consequent heating. They found that, in general, the electrical resistivity increases with both temperature and hydrogen partial pressure, although in a major grade for the first one, evidencing that the hydrogenation process should not significantly affect the design of the proposed heating system.

In spite of the importance of these critical issues, as mentioned before, and the availability of a wide variety of techniques for the determination of these parameters, only a few manuscripts address in detail these concepts for composite-based Pd membranes, comparing the effects of using diverse supports (i.e., ceramic or metallic ones), surface modification treatments (i.e., incorporation of diverse materials as intermediate layer), or the most recent advances for the palladium thin layer incorporation. The research group headed by Tosti analyzed the strain of unsupported Pd-Ag membranes at diverse temperatures and pressures under thermal and hydrogenation cycling, observing that an increase in temperature provokes an expected material elongation, but under hydrogen presence an equivalent variation of temperature involves a contraction effect. In this manner, below 200 °C the hydrogen presence prevails over the conventional temperature effect [166]. On the other hand, one of the most complete studies about adherences of thin films for Pd-based membranes was carried out by Huang et al. [32]. They addressed the adhesion of palladium thin films prepared by conventional electroless plating over tubular ceramic supports modified with an intermediate layer of Al_2O_3 or ZrO_2 . The

membranes were prepared in different laboratories from Germany and China. The characterization of the Pd film adhesion was carried out through five different methods: cross-cut, thermal-shock, hydrogen embrittlement, pull-off, and pressure-tolerating tests. They affirmed that the use of a single method for adhesion determination may give weakness or wrong results, being necessary to confirm the experimental data through diverse techniques. After the complete study, they indicated that roughness in porous supports determines the adherence of the films, being the presence of larger pores more favorable for increasing the adhesion of the palladium coating and, consequently, the mechanical resistance of the composite membrane. In Fig. 2.22, adapted from the images presented in the original work, the results obtained after using each technique for three different membranes are summarized: A, B, and C (from the left to the right). As it can be seen, the membrane C, prepared over a rough surface, exhibited the better adherence for the palladium layer, while the other ones presented delamination and weak mechanical resistance. More recently, Wald et al. [167] studied the strength, hardness, and ductility variations after successive hydrogen absorption/desorption cycles of Pd-Ag alloys. They observed the main changes to the mechanical properties occur just after the first hydrogen exposure treatment and the magnitude of the change is function of the silver content in the alloy, decreasing as it increases.

2.4.10 Gas Permeation Measurements

The coatings prepared as thin film membranes always need to be evaluated in terms of permeation capacity, independently of previous characterization carried out. This crucial property will determine the real behavior of the membrane through gas permeation experiments, the most suitable applications for the obtained material, and the recommended limits for operating conditions.

Usually, a first experiment called bubble point test can be employed in order to evaluate rapidly the homogeneity of the film and the presence of defects, cracks, and pinholes at room temperature. This test consists of dipping the membrane into a solution (typically, water or isopropanol solution) and feeding an inert gas (i.e., helium, argon, or nitrogen) from one side of the film at a constant pressure, detecting the formation of bubbles on the contrary membrane surface. In case of preparing dense palladium or ceramic films, the nonappearance of bubbles indicates a good continuity in the metal films and, consequently, the absence of defects, cracks, or pinholes [43, 51, 72, 73]. On the other hand, in case of considering porous ceramic films, this test provides a qualitative useful information about porosity homogeneity, being possible to detect defects from areas where a great amount of big bubbles are generated. Jakobs and Koros presented the use of this technique in the 1990s as an easy, fast, and inexpensive method to determine both maximum pore size and pore size distribution of diverse ceramic membranes [168], while Reichelt extends the application of this techniques on large membrane areas up to 1 m² [169]. From these first applications, many authors include similar experiments

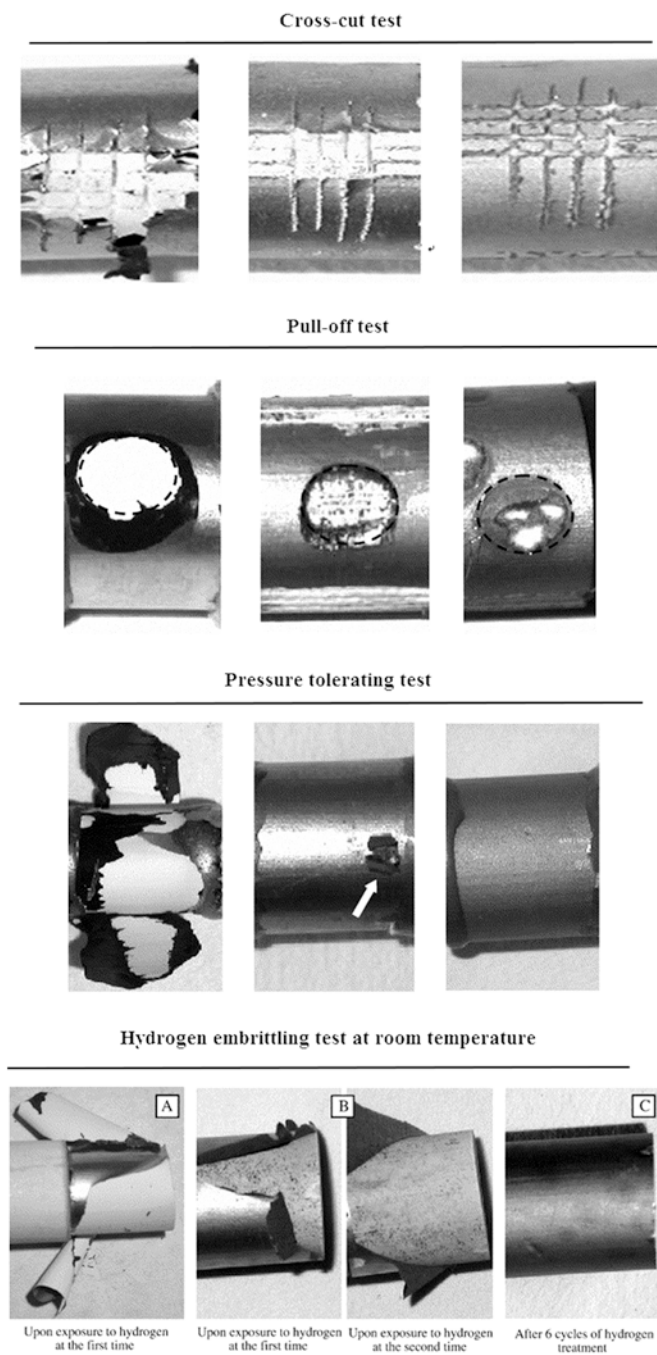


Fig. 2.22 Mechanical experiments over three different composite Pd-ceramic membranes (A, B, and C) prepared by ELP: cross-cut, pull-off, pressure tolerance, and H_2 embrittlement tests. Adapted from [32]

prior to analyzing the permeation behavior at operating conditions, i.e., high temperature or gas mixtures in feed stream.

After these preliminary experiments, real gas permeation measurements are usually carried out at operating conditions in order to determine the real behavior of the membrane in terms of permeated flux, selectivity, and resistance of the material. The effect of pressure, temperature, and feed composition are the most common parameters analyzed in these cases.

The influence of pressure on the membrane behavior is determined by representing the permeate flux versus the pressure, which represents the driving force of the permeation process and it is expressed as partial pressure difference between retentate and permeate sides. In case of using palladium-based membranes, all values are referred to the hydrogen content and the experimental data is fitted to the following general expression:

$$J_{H_2} = \frac{p_{H_2} \left(P_{H_2,ret}^n - P_{H_2,perm}^n \right)}{t} \quad (2.1)$$

where J_{H_2} represents the hydrogen permeate flux through the membrane film, p_{H_2} the hydrogen permeability, t the film thickness, P_{H_2} the hydrogen partial pressure in the retentate (subscript “ret”) or the permeate side (subscript “perm”), and n an exponential factor ranged from 0.5 to 1 that represents the rate-controlling step for the permeation process. For completely free-defect palladium films with thickness upper than 1 μm , hydrogen diffusion through bulk metal is the limiting step of the global permeation mechanism and a good fitting can be achieved considering $n = 0.5$, named the expression as the Sieverts’ law [170, 171]. On the contrary, deviations from this general expression are quantified by varying the coefficient between $n = 0.5$ –1 and they can be caused by the presence of defects or additional resistances to the hydrogen permeation process (i.e., problems in the gas phase diffusion or hydrogen dissociation steps) [172].

It is clear that the hydrogen permeation flux can be maximized by increasing the pressure driving force or decreasing the film thickness, but also depends on the membrane permeability (p_{H_2}). This parameter only relays on the film composition and usually is affected by the temperature through an Arrhenius-type dependence [173].

$$p_{H_2} = p_{H_2}^0 e^{\left(-\frac{E_H}{RT} \right)} \quad (2.2)$$

Besides pressure, temperature, presence of defects, membrane composition, and film thickness, the permeation flux can also be affected by the gas feed composition. All these effects are typically analyzed from experimental data representation as depicted in Fig. 2.23, reproduced from the original work presented by Sanz et al. [43]. Figure 2.23a shows a reasonable good fitting of permeation data to the Sieverts’ law ($n = 0.5$) and the temperature effect on the hydrogen permeability (obtained from the diverse slopes in fitting equations). Figure 2.23b represents the

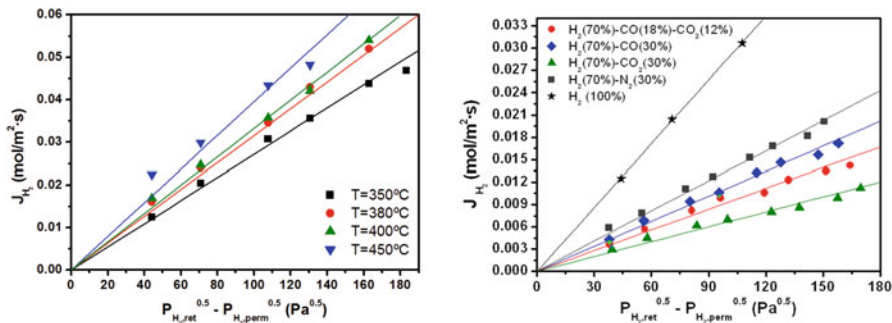


Fig. 2.23 Conventional representation of H₂ flux vs. pressure difference accordingly the Sieverts' law for determination of permeation behavior of Pd membranes: (a) temperature effect and (b) influence of feed composition. Adapted from [43]

influence of carrying out the permeation experiments with diverse feed gas composition on the obtained hydrogen permeability. As it can be observed in the last case, the presence of carbon dioxide and carbon monoxide in the feed stream clearly affect to the permeation process, reducing the hydrogen flux through the thin palladium film at analogous operating conditions.

Finally, selectivity needs to be also determined to evaluate the quality of the membrane films. As an example, only hydrogen can permeate through dense palladium or palladium alloys coatings, although it is usual to find some residual amounts of other gases from the feed stream in the permeate, mainly due to intrinsic defects or membrane deterioration with time. In order to determine the hydrogen selectivity, researchers usually differentiate between ideal separation factor and “real” selectivity.

The first parameter, ideal separation factor, is calculated from total permeate fluxes when hydrogen and other inert compounds, typically helium or nitrogen, are fed to the membrane module separately, being denoted as:

$$\alpha_{ideal} = \frac{J_{H_2}^{perm}}{J_i^{perm}} \quad (2.3)$$

This ideal separation factor is usually defined as the maximum capability of the membrane for separating compounds, and it is widely accepted to present this value for comparison of diverse membranes.

On the other hand, real selectivity is expressed as the ratio between the hydrogen (y_{H_2}) and the inert gas (y_i) molar fractions in permeate and retentate streams. This parameter determines the separation efficiency of a membrane at real operation conditions when diverse compounds are fed simultaneously.

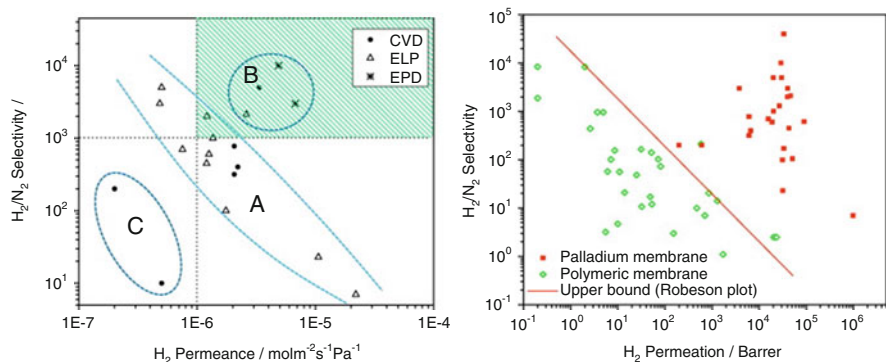


Fig. 2.24 Relationship between ideal H_2/N_2 selectivity and H_2 permeance for diverse membranes: (a) Pd-based membranes prepared by different techniques and (b) comparison of metallic and polymeric membranes. Adapted from original figures in [17]

$$\alpha_{\text{real}} = \frac{\frac{y_{H_2}^{\text{perm}}}{y_i^{\text{perm}}}}{\frac{y_{H_2}^{\text{ret}}}{y_i^{\text{ret}}}} \quad (2.4)$$

In this manner, the selection of a membrane must be carried out attending simultaneously both permeate flux (permeation capability) and selectivity to the compound of interest (separation potential). Figure 2.24 shows different representations for comparing diverse membranes through these permeation properties, permeance and H_2 selectivity. Figure 2.24a compares similar Pd-based membranes prepared by diverse techniques, while Fig. 2.24b compares the permeation behavior of palladium and polymeric membranes.

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