A Comprehensive Performance Assessment Study of Pilot-Scale Pd and Pd/Alloy Membranes under Extended Coal-Derived Syngas Atmosphere Testing

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Abstract

The present study encompasses the results of a comprehensive performance assessment of different pilot-scale Pd/Alloy composite asymmetric membranes under long-term coal-derived syngas atmosphere testing. The membranes were developed and tested first at the CIMS-WPI laboratory under pure H₂ and later at NCCC under a mixture of N₂/H₂ and H₂ enriched syngas coming from a TRIGTM gasification system. Thirteen membranes were examined for 4275 h and classified in four types: Pd, Pd/Au, Pd/Pt and Pd/Au/Pt membranes. Their respective H₂ permeance and purity profiles, permeance difference under pure hydrogen and syngas conditions as well as stability of operation were assessed. The membranes showed good stability in syngas although exhibiting an initial drop in permeance when compared to that under pure hydrogen. Pure Pd membranes displayed the highest permeability, but showed pinholes after being exposed to syngas. Pd/Pt membranes showed a reduced permeance drop under syngas conditions, indicating sulfur resistance properties. Furthermore, Pd/Au/Pt membranes, presented for the first time in the literature, displayed stable permeance and purity profile. The inhibition of the initial permeance drop and the long-term operation of these ternary membranes were demonstrated. Finally, Pd/Au membranes were shown to display the most stable permeance and purity characteristics. In this case, the initial permeance drop was significantly reduced, exhibiting the lowest decline amongst all cases considered. It is hypothesized that Au may act as a patch paste blocking defects on the Pd layer.

Keywords

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1. Introduction

Hydrogen, a major component of the petrochemical and chemical industry, is commonly used for the hydrogenation, hydroalkylation, hydrodenitrogenation and hydrodesulfurization of fossil fuels. In addition, its utilization has become significant in the energy field, where the search of an alternative, clean and stable energy carrier and storage medium is imperative. Hydrogen is currently produced mainly by methane steam reforming (MSR) and water gas shift (WGS) reaction. These processes yield hydrogen mixed with byproducts such as CO, CO₂ and CH₄, which make the purification of hydrogen essential.

According to Koros et al. [1] the two main challenges for the large-scale application of a gas separation technology are: the need of high permselectivity and productivity as well as maintaining these properties in the presence of aggressive feeds; all of these under economic competitiveness conditions. Compared with pressure swing adsorption (PSA) and cryogenic distillation, the use of membranes reduces the costs of hydrogen production [2]. Membrane technology also requires fewer moving parts and has compact modules compared to other technologies [3]. Therefore, membranes are strong candidates to perform the purification of H₂. Specifically, palladium membranes are ideal due to their capability of producing ultrapure H₂ with large fluxes and high recovery rates. Additionally, Pd membranes can be used for process intensification purposes such as in catalytic membrane reactors (CMRs) [4,5].

Before considering any viable expansion possibilities of the range of industrial applications of Pd-based membranes, it is necessary to conduct comprehensive large-scale studies (20-40 Nm³h⁻¹) under actual industrial conditions [6]. Indeed, only a few studies have dealt with such an assessment in a non-controlled environment. For instance, Defalco et al. [7] and Shirasaki et al. [8] used a premixed syngas formed by a previously “contaminant-treated” and desulfurized industrial cylinder gas. Furthermore, at the Center for Inorganic Membrane Studies at Worcester Polytechnic Institute (CIMS-WPI), our group [9] studied the behavior of pilot-scale Pd membranes in a catalytic membrane reactor for the water gas shift (WGS) reaction. Industrial cylinder gas was used to feed CO, CO₂, H₂ and H₂O into the reactor. Even though these represent the major components in a WGS reaction system, impurities and intermediates might affect the performance of the membrane. Therefore, more realistic test settings are required to evaluate the performance of Pd membranes. Indeed, actual coal-derived syngas contains contaminants such as sulfuric components which, can cause the membrane to fail even when found at small traces [6]. Some of the contaminants present in actual coal-derived syngas include: H₂S, COS, NH₃, HCN, C₂ hydrocarbons, poly aromatic hydrocarbons, halides, heavy metals, tellurides, alkalis metals, phosphorous and others [6]. To the best of our knowledge, detailed comprehensive studies on the effect of

these contaminants on the performance of Pd membranes under industrial conditions have not yet been reported in the pertinent literature.

On the other hand, membrane poisoning is an issue that has been intensively studied. To reduce poisoning, different Pd-rich membranes such as Pd/Cu [10], Pd/Ag [11] and Pd/Au [12,13,14] have been tested. In particular, at the CIMS-WPI, we studied the performance of pilot scale Pd/Au membranes under actual coal derived syngas conditions [6,14]. It was found that the H₂ permeance dropped initially when syngas was fed into the membrane module. However, the stability of the membrane remained constant for 200 h. The Pd/Au membrane was capable of achieving a H₂ purity of 98.89% during the entire test. Later [14], it was shown that the permeance of the poisoned Pd/Au membranes could be recovered to their original value after exposure to pure H₂ at 450°C. Motivated by the above preliminary research efforts, the development of a more comprehensive performance analysis framework allowing the derivation of new results to complement and refine the ones of our previous studies represents a natural subsequent step towards the goal of enhancing our understanding of the behavior of pilot-scale Pd and Pd/Alloy membranes under long-term coal-derived syngas atmosphere testing. It should be pointed out that membranes previously reported by our group along with new membranes are included in the present study to further strengthen statistical inference and reliability of the performance assessment results derived within the proposed framework. All membranes were classified in four groups: pure Pd, Pd/Au, Pd/Pt and Pd/Au/Pt membranes in order to understand the effect of the alloy on the properties of the membranes. The investigation includes tests under pure H₂, H₂/N₂ mixed gas, and actual coal derived syngas. The H₂ permeance, H₂ purity, stability characteristics of each membrane as well as the effects of CO, CO₂ and H₂ on membrane performance are comprehensively examined, comparatively assessed and discussed.

2. Materials and Methods

2.1. Membrane Preparation

Composite asymmetric membranes were synthesized, as previously described [6], on porous stainless steel (PSS) tubular supports 316L [15] from MOTT Metallurgical with an outer diameter of 0.025 m and a length of 0.254 m. The total porous surface area of the membrane was 200 cm². One end was welded to a 0.076 m long 316L nonporous tube capped at one end and to a 0.356 m long nonporous tube on the other end.

The supports were cleaned with acetone in an ultrasonic bath. The synthesis of the cleaned supports began by oxidizing the support at 600°C for 12 h in air [16]. Activated Al₂O₃ particles were used to grade the previously oxidized supports and were cemented with Pd [17,18]. The surface of the membranes were then activated with SnCl₂-PdCl₂ and then electroless plating of Pd was used to form a dense layer of pure

Pd over the graded supports [19,20,21]. Gold and/or platinum were deposited on the surface of the dense Pd layer by the standard electro deposition method followed by alloying in situ [5,22,23]. The thickness of the membranes was estimated by gravimetric methods. Different Pd and Pd/Alloy membrane thicknesses were used in order to conduct a comprehensive analysis of each alloy. It should be pointed out that these membranes were designed to produce H₂ with purity equal or higher than 99% and a permeance of 15 Nm³m⁻²h⁻¹bar^{-0.5} under syngas conditions.

Table 1 shows the summary of the principal characteristics of all the composite Pd and Pd/alloy membranes synthesized at the CIMS-WPI and the nomenclature used in this study. Thirteen Pd and Pd/alloy membranes were tested first at WPI under pure hydrogen for about 100 hours at 450°C and afterwards were sent to the National Carbon Capture Center (NCCC) in Wilsonville, AL. to be tested under H₂/N₂ mixed gas and syngas conditions at 450°C and 12.6 atm. The total effective testing time for all thirteen membranes was 4275 h. Notice that testing results of membranes labelled with an asterisk (*) have been previously reported; nevertheless, these results are retained and used in the present study to extend the statistical range and strengthen its reliability. Two membranes, M-02^{***} and M-06^{***}, were tested in our laboratory under a controlled mixture of CO, CO₂, H₂O and H₂. Moreover, temperatures ranging between 420-440°C and a maximum pressure of 20 bar were used in this work. Notice also that these membranes were used for a catalytic membrane reactor test on a pilot scale [9] in order to better understand and assess the effect of these major syngas components on the membrane under consideration.

Table 1. Summary of the composite Pd and Pd/alloy membranes

Membrane Nomenclature	Composition and thickness, μm	Testing time, h	Test Setting
M-04b	14(Pd)+0.9(Au)	250	Industrial coal derived syngas and H ₂ and N ₂ mixture
M-08	8.5(Pd)+0.33(Au)+0.1(Pt)	650	
M-09	8.5(Pd)+0.35(Au)+0.06(Pt)	175	
M-10	9.6(Pd)	225	
M-11	5(Pd)+0.8(Au)+0.9(Pd)	350	
M-12	4(Pd)+0.5(Pt)+0.9(Pd)	350	
M-13	4.8(Pd)+0.45(Pt)	150	
M-14	10.3(Pd)+0.3(Au)+0.09(Pt)	725	
M-01 [*]	8.2(Pd)+0.16(Au)	225	
M-03 [*]	10(Pd)+0.2(Au)	275	
M-03b ^{**}	9.6(Pd)	175	
M-04 [*]	13.1(Pd)	250	
M-07 ^{**}	8.7(Pd)+0.5(Au)	475	
M-02 ^{***}	7.4(Pd)	450	Mixture of CO, CO ₂ , H ₂ O and H ₂
M-06 ^{***}	8.3(Pd)	390	

Described in our previous works: [6], [9] and [14]

2.2. Coal-derived Syngas and Membrane Testing

The details of the skid used at WPI were previously described [6,14]. The syngas produced at NCCC comes from an air blown transport integrated gasification (TRIGTM) system fed with powder river basin (PRB) coal. The syngas from the gasifier was cooled down to 400°C and sent to a particle control device (PCD) where the particulates were reduced to 0.1 ppmv [24]. Following the removal of particles, the syngas was sent to a WGS shift reactor to reduce the CO content to <1% followed by a ZnO bed for sulfur removal and then a COS hydrolyser. A H₂S reduction of <1 ppm was achieved with undetectable COS based on GC. The syngas used for testing was mixed with industrial H₂ for enrichment up to 30-40% and to increase the driving force for permeation. Afterwards, the enriched syngas passed through a second ZnO bed. The average syngas feed composition was: H₂: 33%, N₂: 46%, CO<1%, CO₂: 12%, H₂O: balance. For a more detailed description of the syngas composition and preliminary clean up, the reader is referred to CIMS-WPI's previous work [6]. Finally, it should be pointed out that the hydrogen permeate was measured with a rotameter and its composition by a GC (model Simens Maxum II, columns: HysepN and HA-MS for H₂, N₂, CO, and CH₄; HysepN and HysepQ for CO₂ and H₂S; detector was a TCD).

3. Results

3.1. Group 1. Pure Pd Membranes

Group 1 is comprised of pure Pd-based membranes. The characteristics of these membranes were used as the standard-basis in our comparative assessment of the performance of the Pd/Alloy membranes. Five Pd membranes were used for this study with different Pd thicknesses ranging from 7.4-13.1 μm (Table 2).

Table 2. Composition of the pure Pd membranes

Membrane Nomenclature	Composition / μm
M-02 ^{***}	7.4 (Pd)
M-03b ^{**}	9.6 (Pd)
M-04 [*]	13.1 (Pd)
M-06 ^{***}	8.3 (Pd)
M-10	9.6 (Pd)

The H₂ permeance of M-04^{*} and M-10 was tested initially under pure H₂ at WPI and later under H₂/N₂ gas mixture and syngas at NCCC. The respective profiles are shown in Figure 1. In this work, all the permeances shown as a single gray-labeled point represent the average permeance measured at WPI over 100 h. The H₂ permeance under H₂/N₂ atmosphere is shown with the series filled in white, while permeance under hydrogen enriched syngas is shown in solid-black series. Membranes M-02^{***} and M-

M-06^{***} were used in CMRs to perform the WGS with only CO, CO₂, H₂ and H₂O present. Their H₂ permeance was measured before and after the reaction. The reaction proceeded for 450 h and 390 h for M-02^{***} and M-06^{***}, respectively [9]. It should be mentioned that M-03b^{**} was originally synthesized as a Pd/Au membrane (M-03^{*}). However, after testing, M-03^{*} was polished [19] and replated with 2 μm of Pd [14]. It was expected that the mechanical treatment removed the Au layer of the membrane. However, due to intermetallic diffusion, traces of Au might still be present in the membrane or in the support. Therefore, its characteristics [14] were used only for comparison purposes and its permeance was not included in Figure 1.

M-04^{*} showed an initial H₂ permeance of 23.2 Nm³m⁻²h⁻¹bar^{-0.5} at WPI. At NCCC however, afterwards the flow rapidly declined to 11.6 Nm³m⁻²h⁻¹bar^{-0.5} and further down to 8.1 Nm³m⁻²h⁻¹bar^{-0.5} after 200 h. The hydrogen permeance experienced a drop of 55% compared to its initial value. After removal, the surface of the membrane was covered with a thick black layer.

The permeance of M-10 at 450°C measured at WPI under pure H₂ was 29.2 Nm³m⁻²h⁻¹bar^{-0.5} with a H₂/He selectivity >2500. At NCCC, M-10 was tested for a total of 230 h under H₂/N₂ and syngas atmosphere. The membrane first dwelt under H₂/N₂ where the H₂ permeance declined compared to the value measured under pure H₂ at WPI. After 40 h under H₂/N₂, the average permeance decreased by 70%. Upon syngas introduction, no significant decrease of the H₂ permeance was observed indicating that H₂ permeance inhibition (mostly due to surface contamination) occurred in the H₂/N₂ mixture. The permeance of M-10 membrane was 5.8 Nm³m⁻²h⁻¹bar^{-0.5} and remained constant in syngas for 120 h (80% loss compared to the level observed at WPI). After this time, the flow started to increase abruptly indicating the opening of pinholes resulting in a loss in selectivity.

As previously reported [14], the WPI permeance of M-03b^{**} was 17.7 Nm³m⁻²h⁻¹bar^{-0.5}. The membrane showed a permeance drop to 11.1 Nm³m⁻²h⁻¹bar^{-0.5} under syngas. The permeance drop corresponded to 37% of the original permeance. This reduction in permeance was significantly lower than that of M-04^{*} and M-10. It is important to notice that the membrane thickness of M-03b^{**} was the same as M-10 but thinner than M-04^{*}. This meant that the permeance drop observed in these membranes did not depend on the thickness of the Pd layer and was mainly due to surface contamination. The lower permeance drop in M-03b^{**} could be attributed to the presence of Au traces within the Pd structure and/or the support.

Before being tested as CMRs, M-02^{***} and M-06^{***} were tested at 420°C and displayed H₂ permeances of 21.7 and 21.9 Nm³m⁻²h⁻¹bar^{-0.5}, respectively [9]. The WGS reaction took place for 450 h and 390 h for M-02^{***} and M-06^{***}, respectively. After the reaction, the membranes had H₂ permeances of 18.9 and 19.4 Nm³m⁻²h⁻¹bar^{-0.5}, respectively. This corresponded to a permeance drop of 13% and 11%, respectively. As our group reported previously [9], the reason for the permeance decline was due to intermetallic diffusion caused by uneven temperature distribution, which was higher than 450°C, and not because of the presence

of CO, CO₂ and H₂O. The permeance drop under syngas of MA-04* and MA-10 was significantly larger than that of M-02*** and M-06*** and this phenomenon occurred within a shorter period of time. This behavior suggested that the presence of CO, CO₂ and H₂O did not affect the stability of pure Pd membranes and that the permeance drop was caused by the presence of other contaminants.

Figure 1. H₂ Permeance of pure Pd membranes as a function of time.

The H₂ purity profiles of pure M-04* and M-10 are shown in Figure 2. The hydrogen purity of M-10 under syngas was 99.7% that remained constant for 120 h; the purity decreased however to 77.9% after 227 h. The H₂ purity of M-10 did not seem to depend on the gas composition. M-04* had a more stable purity profile throughout the test with an average value of ~98%. The H₂ purity was >99.2% at the beginning of the test and declined to 96.8% after 240 h. The purity of M-04* seemed to be lower under H₂/N₂ mixed gas than that under syngas conditions. M-04* was more robust and had longer stability under syngas conditions than M-10. The permeance of M-04* decreased by 50% from its original value while M-10 decreased by 75%. The reason was the thicker dense Pd film of M-04* (13.1 μm) when compared to that of M-10 (9.6 μm). It is important to mention that although the permeance of these membranes dropped considerably, their performance was still competitive. According to Oyama et al. [25] membranes with

permeances $>6 \text{ Nm}^3 \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-0.5}$ and with H_2/N_2 selectivities >1000 are within or above a Robeson upper boundary limit of Pd membranes.

Figure 2. H₂ Purity produced by pure Pd membranes as a function of time.

Although, the previous Pd membranes showed an H₂ purity drop under syngas; M-03b^{**} had H₂ purities greater than 99.4% that remained constant for 175 h [14]. The performance of M-03b^{*} is an exception of the already seen Pd membranes suggesting that the previously deposited Au still affected the performance of this membrane.

Pure Pd membranes failed after ~200 h of operation under syngas conditions. The harsh environment reduced their stability causing the formation of pinholes on the surface of the membrane as shown in Figure 3. The SEM picture shows the surface morphology of M-10 in the deteriorated area. The presence of a crack caused by the long-term exposure of syngas or H₂S could be clearly seen. These defects appeared to a lower extent in M-04^{*} because of its thicker Pd layer. Studies on Pd membranes were usually conducted for short periods of time under clean gas conditions [26,27]. However, as demonstrated here, it was necessary to test the membranes for a minimum of 200 h under industrial conditions to ensure their stability. Ryi et al. [28] attempted to increase the stability of pure Pd membranes within this timeframe. They showed that pure Pd membranes tested under pure H₂ conditions tended to fail before

200 h. Furthermore, the H₂ purity produced by M-06^{***} [9] was 99.97% at 15 bar, but declined when the pressure was increased to 20 bar. This suggested the existence of pinholes that allow more impurities to penetrate the Pd layer at higher pressures.

Figure 3. SEM image of a crack formed at the Pd surface layer of M-10.

3.2. Group 2. Pd/Au Membranes

Group 2 is composed of asymmetric composite membranes formed by Pd and on top a layer of Au. Different thicknesses, shown in Table 3, were used for testing the features of these membranes. M-01^{*} had a dense Pd layer of about 8.2 μm thickness with a topmost layer of Au with a thickness of 0.16 μm. M-03^{*} had a Pd thickness of 10 μm and 0.2 μm of Au. M-07^{**} consisted of an 8.7 μm Pd layer and an 0.5 μm Au layer. Both M-01^{*} and M-07^{**} had a similar palladium thickness but different amounts of Au for comparison. Membrane M-04b consisted of a dense 14 μm Pd layer and was additionally covered with an 0.9 μm Au layer. Notice that M-04b was designated as M-04 before Au was deposited and was tested as a pure Pd membrane in the previous section. M-04b had a similar Au load as M-07^{**} but twice as much Pd. Finally, M-11 consisted of a dense Pd layer of only 5 μm covered with an 0.8 μm Au layer and an 0.9 μm Pd layer on top of the Au layer.

Table 3. Pd-Au asymmetric membrane composition.

Membrane Nomenclature	Composition / μm
M-01 [*]	8.2(Pd) + 0.16(Au)
M-03 [*]	10(Pd) + 0.2(Au)
M-07 ^{**}	8.7(Pd) + 0.5(Au)
M-04b	14(Pd) + 0.9(Au)
M-11	5(Pd) + 0.8(Au) + 0.9(Pd)

The permeance of the Pd/Au membranes was tested under H₂/N₂ mixture and syngas atmospheres. Figure 4 shows the permeance of these membranes as a function of time. The permeance of the membranes under H₂/N₂ mixture and under syngas is shown for all membranes including the WPI permeance shown as a single gray-labeled point.

M-01^{*} showed an initial permeance at WPI of 28.2 Nm³m⁻²h⁻¹bar^{-0.5} and dropped to 21 Nm³m⁻²h⁻¹bar^{-0.5} under H₂/N₂ and to 8.5 Nm³m⁻²h⁻¹bar^{-0.5} under syngas [6]. M-07^{**} had a WPI permeance of 29.2 Nm³m⁻²h⁻¹bar^{-0.5}. Under H₂/N₂ atmosphere, the membrane showed a permeance of 9.5 Nm³m⁻²h⁻¹bar^{-0.5}. The permeance increased after switching to syngas, and then decreased to reach a steady average permeance of 13 Nm³m⁻²h⁻¹bar^{-0.5}. M-07^{**} was tested for 470 h producing 0.63 kg of H₂ per day at the end of testing. M-04b had a WPI permeance of 11.4 Nm³m⁻²h⁻¹bar^{-0.5} with a H₂/He selectivity >2700. This Pd/Au membrane was tested for 250 h under H₂/N₂ mixtures and syngas atmospheres. After 40 h in H₂/N₂ mixture, the permeance had a steady permeance which corresponded to a 25% decrease in permeance. Upon syngas introduction, the H₂ permeance decreased 37%.

M-11 showed a WPI permeance of 22.7 Nm³m⁻²h⁻¹bar^{-0.5} with a H₂/He selectivity >2207. M-11 was tested for a total of 350 h. The H₂ permeance of M-11 declined by 36% under an H₂/N₂ mixture and, upon the introduction of syngas, it gradually decreased further. M-03^{*} was not tested under pure H₂ at WPI therefore its permeance was not included in Figure 4. However, its permeance was the same under H₂/N₂ and syngas (17.6 Nm³m⁻²h⁻¹bar^{-0.5}) conditions. The membrane remained stable for 100 h, but an increase in H₂ flux occurred along with a large leak [6].

Similar to pure Pd membranes, Pd/Au membranes exhibited an initial drop in permeance as soon as they came in contact with the N₂/H₂ mixture. This phenomenon supported the fact that some contaminants were adsorbed on the piping walls and stripped out with the hot N₂/H₂ mixture. The Au content on the membranes reduced the H₂ permeance. For instance, M-07^{**} with a thinner Au layer (0.5 μm) displayed a permeance 40% greater than M-04b (0.9 μm). In the case of M-04b and M-11, both membranes had a similar Au load; however, M-11 had an upper Pd layer, which could have improved its permeance. Additionally, it is important to notice that M-11 had a thinner Pd layer. M-04b was subjected to syngas atmosphere and H₂S treatments after 120 h of testing. H₂S was introduced at a concentration of 10.6 ppm leading to a reduction of H₂ permeance to 3 Nm³m⁻²h⁻¹bar^{-0.5}. After 200 h, the H₂S input was stopped and the membrane recovered its initial H₂ permeance of 7.2 Nm³m⁻²h⁻¹bar^{-0.5} in about 30 minutes.

The addition of Au did not seem to affect the initial WPI permeance when compared with pure Pd membranes. The reason was that the active sites of the Pd layer were available for H₂. Gold did not seem to block these sites, suggesting that intermetallic diffusion of Au into Pd occurred. In addition, it could be seen that Pd/Au membranes experienced a fast loss in permeance at first, most probably due to the adsorption of unknown contaminants on the surface and no further significant permeance loss occurred

indicating a low or negligible bulk contamination. Surface poisoning, as previously described by Chen and Ma [13] affected the permeance of the membrane in two stages: surface and bulk sulfidation. First, the surface of the membrane was contaminated by H_2S , failing to separate H_2 . This was evidenced by the initial decrease in permeance (from the permeance measured at WPI to the initial sulfur exposure). The second stage involved the bulk deterioration of the Pd film, which in the case of Pd/Au was not present causing no further permeance drop.

Figure 4. H_2 Permeance of Pd/Au membranes as a function of time.

The purity of the Pd/Au membranes was more stable throughout the test as shown in Figure 5. The H_2 permeance of the Pd/Au membranes did not depend on whether the feed gas was H_2/N_2 or syngas. The H_2 purity produced by the M-01* membrane stayed above 99.89% during the entire 220 h of testing. After removal from the test, no carbonaceous deposit was observed on the membrane surface. M-07** had a rather stable purity ~99.9% throughout the measurements. M-04b showed that the introduction of H_2S between 120 h and 200 h had no effect on H_2 purity. The resulting H_2 purity under syngas during 250 h was >99.5%. M-11 had a stable H_2 purity profile of 99.5%. These results showed that Pd/Au membranes were stable in a syngas atmosphere for over 200 h, in contrast with pure Pd membranes.

Under syngas, the H_2 purity produced by these membranes remained constant, but the permeance decreased. This suggested that the active sites of the surface became poisoned at first, decreasing the H_2 permeance. In the case of pure Pd membranes, the bulk Pd layer was further poisoned, damaging it and generating defects. However, for Pd/Au membranes, while the surface became contaminated, Au diffused towards the defects on the bulk preventing the development of pinholes. Indeed, Au seemed to fill and cover any pinholes or defects produced at the Pd layer, acting as a patch paste.

Figure 5. H_2 Purity produced by of Pd/Au membranes as a function of time.

3.3. Group 3. Pd/Pt Membranes

Group 3 is composed of asymmetric membranes formed by Pd with Pt on the top. Although few studies have been reported on Pd/Pt membranes; it is suggested that Pt has H_2S resistant properties that can be exploited to improve the resistance of Pd/Alloy membranes [29,30,31]. Kajiwara et al. showed a small change on the lattice structure of Pt (0.39 to 0.35 nm) after sulfidation compared to that of Pd (0.39 to 0.65 nm) [32]. The reported Pd/Pt membranes had cracks allowing the leak of other gases to pass through. For the purposes of this investigation, two membranes were fabricated with compositions shown in

Table 4. M-12 consisted of a 3.9 μm thick dense Pd layer, which was additionally covered, with an 0.5 μm Pt layer and an 0.9 μm Pd layer on top of the Pt layer. M-13 membrane was plated with 4.8 μm of Pd and 0.45 μm of Pt on top, to produce a Pd/Pt asymmetric membrane. Notice that this is the first time that

the results of a performance assessment of Pd/Pt membranes are reported in the literature under actual coal derived syngas.

Table 4. Pd/Pt membrane composition.

Membrane Nomenclature	Composition / μm
M-12	4(Pd) + 0.5(Pt) + 0.9(Pd)
M-13	4.8(Pd) + 0.45(Pt)

Figure 6 shows the H_2 permeances at WPI, under H_2/N_2 mixture and syngas of the Pd/Pt membranes as a function of time. The H_2 permeance of M-12 (Pd/Pt/Pd) measured at WPI was $15.7 \text{ Nm}^3\text{m}^{-2}\text{h}^{-1}\text{bar}^{-0.5}$ with a H_2/He selectivity of 393. Although, M-12 had a high platinum content close to its surface; it still displayed a high H_2 permeance. This Pd/Pt/Pd membrane was tested for a total of 350 h under H_2/N_2 and syngas atmospheres. The membrane first dwelt under H_2/N_2 where the permeance declined by 36%. Upon syngas introduction, a slight decrease in permeance was observed reaching a minimum of $8.4 \text{ Nm}^3\text{m}^{-2}\text{h}^{-1}\text{bar}^{-0.5}$. At 160 h, the flow started to increase abruptly indicating the opening of pinholes and a loss in selectivity. The feed gas was alternated between H_2/N_2 and syngas but the permeance kept increasing independently of the composition of the feed.

The H_2 permeance of M-13 measured at WPI was $16.5 \text{ Nm}^3\text{m}^{-2}\text{h}^{-1}\text{bar}^{-0.5}$ with an ideal selectivity of 590. At NCCC, M-13 was tested for a total of 150 h. The permeance of the membrane declined by 59% under H_2/N_2 , as seen in previous membranes. The permeance of M-13 also remained relatively constant in syngas after 150 h of testing. Unfortunately, the gasifier' operation stopped and further testing was not performed in order to observe whether this Pd/Pt membrane also failed at times >150 h. Since, M-12 had a Pd layer on top of the Pt film; its H_2 permeance was slightly higher than M-13.

The magnitude of the H_2 permeance of the Pd/Pt membranes was lower when tested at WPI than those composed of pure Pd. This was the result of covering the surface of the Pd layer, where the active sites were located with Pt. Once the membrane became poisoned pure Pd and Pd/Pt membranes showed permeances of the same magnitude. This indicated that while the active sites of the surface of pure Pd membranes became occupied by the contaminant; Pd/Pt membranes reduced the effect of the contaminant. Pt might have an effect on reducing poisoning, but further investigation is required.

Figure 6. H₂ Permeance of Pd/Pt membranes as a function of time.

Figure 7 shows the H₂ purity of the Pd/Pt membranes as a function of time. M-12 showed an initial H₂ purity of 98% that remained stable for 100 h under H₂/N₂. After feeding syngas for about 50 h; the purity of the membrane increased to 99%. At this moment, the H₂/N₂ was introduced again, and the purity experienced a steady drop to 93%. The feed gas was changed again to syngas where the purity seemed to recover. However, the decline in purity continued until the end of the test. M-13 was tested for a shorter time period. This membrane was more stable and produced a higher H₂ purity than that of M-12. Under H₂/N₂ atmosphere the membrane showed an H₂ purity of 99%, while under syngas, the membrane produced H₂ with a purity of >99.5%. Notice that the produced H₂ purity of M-12 in Figure 7 was similar to M-10 (pure Pd) in Figure 2. Both membranes remained stable for about 150 h and afterwards, a sudden loss of selectivity occurred. This suggested that Pt did not patch the defects in the Pd layer.

Figure 7. H₂ Purity produced by Pd/Pt membranes as a function of time.

3.4. Group 4. Pd/Au/Pt Membranes

Group 4 is comprised of membranes formed by Pd, Au and Pt. Ternary alloy membranes such as Pd/Cu/Ni [33], Pd/Ag/Cu [34] and Pd/Cu/Au [35] have been extensively reported. However, performance assessment results of Pd/Au/Pt membranes have never been reported in the pertinent literature. It was expected that the combination of these metals will highlight the properties of Au and Pt in their capacity to enhance the sulfur resistance of the membranes.

Different compositions were used for testing the characteristics of these metals as shown in Table 5. M-08 and M-09 had similar palladium and gold loads (close to $\sim 8.5 \mu\text{m}$ of Pd and $\sim 0.34 \mu\text{m}$ of Au), but a different platinum load with $0.1 \mu\text{m}$ and $0.06 \mu\text{m}$, respectively. M-14 membrane had a $10.3 \mu\text{m}$ of Pd, and $0.3 \mu\text{m}$ layer of Au on top and an $0.09 \mu\text{m}$ layer of Pt.

Table 5. Pd/Au/Pt membrane composition.

Membrane Nomenclature	Composition / μm
M-08	8.5(Pd) + 0.33(Au) + 0.1(Pt)
M-09	8.5(Pd) + 0.35(Au) + 0.06(Pt)
M-14	10.3(Pd) + 0.3(Au) + 0.09(Pt)

The H_2 permeances of the Pd/Au/Pt membranes are shown in Figure 8. The H_2 permeances measured at WPI are shown in a single- point format as previously indicated, and as a function of time under H_2/N_2 and syngas. M-08 displayed a H_2 permeance at WPI of $17.4 \text{ Nm}^3 \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-0.5}$ with a H_2/He selectivity >1000 . At NCCC, M-08 was tested for 460 h; under H_2/N_2 , the permeance declined from its initial WPI value. The permeance partially recovered after 13 h of testing. Upon syngas introduction, the permeance first decreased but remained constant. A gasifier trip occurred and a H_2/N_2 mixture was introduced to preserve the membrane. Under H_2/N_2 , the permeance recovered, showing a permeance close to the one measured at WPI. The recovery of the permeance might be the result of the Pt addition, yet this hypothesis needs further verification. Due to the long time needed to repair the gasifier, the membrane was cooled down to room temperature and remained at atmospheric temperature and pressure. After the gasifier was repaired, a second test was started. The membrane dwelt under an H_2/N_2 atmosphere and the permeance was similar as before the cooling down. The permeance under syngas was $11 \text{ Nm}^3 \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-0.5}$ and remained stable. This permeance was similar to the one measured during the first 60 h in syngas. Unfortunately, a second gasifier trip occurred and the run was terminated.

The H_2 permeance of M-09 at WPI was $28.4 \text{ Nm}^3 \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-0.5}$ with a H_2/He selectivity >680 . M-09 was tested for a total time of 169 h. The membrane first dwelt under H_2/N_2 where the permeance declined compared with its initial WPI value. After 40 h under H_2/N_2 the average permeance decreased by 65%. The introduction of syngas had no significant effect on the permeance. The permeance of M-09 was $9.5 \text{ Nm}^3 \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-0.5}$ and remained constant after 123 h under syngas. The feed was switched back to H_2/N_2 where the membrane exhibited the same permeance as before feeding with syngas.

The WPI permeance of M-14 was $22 \text{ Nm}^3 \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-0.5}$ with an ideal selectivity of 732. At NCCC, M-14 was tested for 718 h. The membrane first dwelt under H_2/N_2 where the permeance decreased compared to the levels previously measured at WPI. Under H_2/N_2 , the average permeance had a permeance drop of 60%. Syngas was fed afterwards and maintained for 578 h. During the first 200 h the H_2 permeance increased slightly followed by a sustained average permeance of $10.5 \text{ Nm}^3 \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-0.5}$ until the end of the test.

Compared to pure Pd membranes, the ternary alloy displayed WPI permeances with a similar magnitude. Although, Pt slightly reduced the permeance of the Pd/Pt membranes; its effect was not evident in this group. The difference was due to the smaller amount of Pt deposited onto these ternary membranes. Au, on the other hand, did not seem to interfere with active sites of the Pd layer. Furthermore, compared with pure Pd membranes, the permeance of Pd/Au/Pt membranes did not deteriorate with time. The effect could be attributed to the Au present in the membranes.

Figure 8. H₂ Permeance of Pd/Au/Pt membranes as a function of time.

The purity produced by the Pd/Au/Pt membranes is shown in Figure 9. M-08 produced H₂ with a purity of >99.8% throughout the test. The H₂ purity produced by M-09 was higher under syngas than the purity under H₂/N₂. For instance, the average purity of the H₂ produced under H₂/N₂ and syngas was 96.9 and 98.8%, respectively. M-14 produced H₂ with purity >99% but had a slight but steady decline throughout the 700 h of operation. Notice that the statistical outliers present in the above figure can be attributed to inevitable errors on the experimental measurements involving a rather complex process system such as the one under consideration. However, the main/central trend depicted in the membrane's performance profile is clearly identifiable, thus reliably supporting the aforementioned conclusions.

Compared with pure Pd membranes, the ternary alloy showed superior stability for producing highly pure H₂. Although M-09 did not reach a purity of 99%, it remained stable throughout the test. The cause of the lower selectivity of M-09 could be a small defect present in the membrane. This defect did not grow since the H₂ purity did not decrease. This suggests that Au stabilized the pinhole and did not allow its deterioration. The effect of Pt on this pinhole stabilization could not be concluded since, leak growth was observed in one of the Pd/Pt membranes.

Figure 9. H₂ Purity produced by Pd/Au/Pt membranes as a function of time.

4. Discussion

4.1. Overall performance of the Pd and Pd/Alloy membranes

The performance of the Pd, Pd/Au, Pd/Pt and Pd/Au/Pt composite asymmetric membranes under coal-derived syngas was evaluated in four categories: H₂ permeance, permeance drop compared to the value measured at WPI under pure H₂, quality of produced H₂, and stability of the membrane. Although, each membrane performed differently, the average value of the Pd and Pd/Alloy groups was used to evaluate their characteristics. Notice that Table 6 shows the characteristics of 11 membranes, which are the most representative for this study.

Permeability was used as a parameter for evaluation, since it provided a better understanding of the intrinsic properties of the material that allowed/promoted hydrogen permeation. Permeability excluded the resistance provided by the thickness of the material. The average permeability of the membranes presented in this work, shown in Table 6, had the following order Pd > Pd/Au/Pt ≥ Pd/Au > Pd/Pt. Pure palladium displayed the highest permeability, while all composite Pd/Alloy membranes showed a reduced permeability. This was reasonable since Pd was the active material that catalyzed the dissociation and thus the transport of H₂. The permeability of the Pd/Au membranes under syngas was 19% lower than that of pure Pd membranes. Platinum seemed to result in a deterioration of the membrane's permeance profile.

For instance, the Pd/Pt membranes displayed the lowest permeability, 58% lower than pure Pd membranes. As explained before, Pt blocked the active sites of the Pd layer and therefore resulted in lower activity. For the case of the ternary composite membranes, their H₂ permeability decreased by only 11%. The drop in permeability was lower than Pd/Pt possibly because of the presence of Au and the smaller Pt load.

All Pd and Pd/Alloy membranes showed a permeance drop when in contact with the stream containing traces of different contaminants such Mg, Na, Hg, S, etc. These contaminants were previously investigated and were found to be desorbed at the equipment walls [14]. The permeance drop was estimated from the initial permeance displayed at WPI and the average permeance shown at NCCC. The permeance drop due to mass transfer resistance of gas mixtures is negligible and was estimated to be in the range of 0.6-1.6%. The order of membranes, from the lowest permeance drop to the highest, is as follows: Pd/Au > Pd/Pt > Pd/Au/Pt > Pd. Pure Pd membranes showed the highest permeance drop. Pd/Au membranes showed the smallest drop followed by Pd/Pt and the ternary membranes. These results suggested that adding alloys helped to protect the active sites of the Pd layer from harsh environments. Alloys seemed to hinder some of the sites where the poison attacked the surface of the membrane.

The maximum H₂ purities produced under actual syngas conditions by the different membranes had the following order: Pd/Au > Pd/Au/Pt > Pd > Pd/Pt as shown in Table 6. The presence of Au improved the H₂ selectivity of the membrane by patching any defects or pinholes on the surface of the Pd layer. On the other hand, the Pd/Pt showed the lowest H₂ purity. The effect of Pt appeared to be harmful to the production of pure H₂. The purity displayed by the ternary composite membrane was similar to Pd/Au. It seemed that even in small amounts, Au had a positive effect on the membrane.

The stability of the membranes was estimated based on the maximum time where the membranes achieved a consistent purity >99% under syngas conditions. Notice that, as shown in Table 6, the time of stability does not necessarily represent the time when the membrane failed in achieving a purity of 99%. In some cases, this time represented the moment when the test was terminated. For instance, the two tested Pd membranes failed in achieving this purity at 49.5 and 182.9 h. Therefore, it was considered that pure Pd membranes failed at 182.9 h, which was the maximum time found in this work. Membranes composed of Pd/Au did not fail during testing. They always displayed purities >99%, so the sole limitation was the testing time. The longest testing time under syngas atmosphere of Pd/Au membranes was 471 h. In the case of Pd/Pt membranes, one membrane failed after only 29 h of testing. The other Pd/Pt membrane did not fail, but its testing stopped after 112 h in syngas. The ternary Pd/Au/Pt membrane showed one failed membrane. This membrane did not reach a purity of 99% from the beginning of the test. The maximum operating time of Pd/Au/Pt membrane was 535.5 h. Therefore, the stability of the tested composite membranes followed the order of Pd/Au > Pd/Au/Pt > Pd > Pd/Pt. This

implied that Au, during intermetallic diffusion, patched the defects that appeared in the Pd layer. Platinum had the opposite effect; it opened cavities within the Pd structure.

Table 6. Characteristics of the different Pd and Pd/Alloy membranes under coal-derived syngas.

Type	Membrane	Permeability ^{a)} , $\text{Nm}^3\text{m}^{-1}\text{m}^{-2}\text{h}^{-1}\text{bar}^{-0.5}$	Maximum H_2 purity, %	Initial permeance drop, % ^{b)}	Time w/ purity >99%, h ^{c)}	Reason of termination
Pure Pd	M-04*	2.21×10^{-4}	99.26	55	49.5	Failed
	M-10	9.03×10^{-5}	99.73	75	182.9	Failed
	Average	1.56×10^{-4}	99.5	65		
Pd/Au	M-01*	1.15×10^{-4}	99.94	33	198.5	Stopped
	M-07**	1.67×10^{-4}	99.93	68	471	Stopped
	M-04b	1.02×10^{-4}	99.88	36	223	Stopped
	M-11	1.19×10^{-4}	99.95	38	293	Stopped
	Average	1.29×10^{-4}	99.93	44		
Pd/Pt	M-12	8.89×10^{-5}	99.69	34	29.3	Failed
	M-13	4.09×10^{-5}	99.07	59	112	Stopped
	Average	6.49×10^{-5}	99.38	46		
Pd/Au/Pt	M-08	1.53×10^{-4}	99.91	28	64.8	Stopped
	M-09	1.06×10^{-4}	98.83	65	N/A	Failed
	M-14	1.55×10^{-4}	99.86	61	535.5	Stopped
	Average	1.38×10^{-4}	99.53	52		

a) Permeability was estimated based on the total metal thickness of the membranes and calculated from the permeance under syngas conditions.

b) The initial permeance drop was calculated from the permeance displayed by the membranes under pure H_2 vs. the permeance under syngas or N_2/H_2 mixture. c) This is the period of time where the membrane displayed a purity >99% under syngas conditions.

4.2. Performance of Au and Pt as membrane composites

It is important to notice that these results represent the actual performance of the membranes under real industrial conditions and therefore the environment was not controlled as in the laboratory. Therefore, further research investigations are undoubtedly warranted in order to have a more conclusive and sound understanding on the characteristics of these membranes. However, based on the performance of the Pd/Au and Pd/Au/Pt membranes shown in this work, the role of Au appears to be 1) a patching paste that cures the defects present at the surface of the membrane, 2) a pinhole stabilizer and 3) an agent that hinders poisoning. Competition of active sites, the Tamman temperature of Au and the Kirkendall effect [36] could certainly contribute to an explanation of the manifested properties.

The Tamman temperature of Au (395°C) is significantly lower than Pd (641 °C). Therefore, operating at 450 °C, places Au into a state of higher molecular mobility than Pd. In asymmetric membranes, at the Au-Pd boundary, the Kirkendall effect takes place. Gold crosses the Au-Pd boundary and diffuses into the Pd layer; while Pd remains relatively motionless within its limits. This effect allows Au to fill in the voids or defects present in the Pd layer like a patching paste. If the defect is significantly big, Au cannot fix the pinhole. However, its deposition at the walls of the defect seems to stabilize it and prevent further growth.

The experiments suggested that Au hindered poisoning of the Pd surface. This could be explained by competition for active sites during adsorption. Some of the sites where sulfur adhered were already occupied by Au preventing a strong attachment to the Pd surface. This was supported by the permeance recovery that Pd/Au membranes showed when treated under pure H₂ at 450°C [14].

Platinum also appeared to hinder poisoning in a similar way as Au did, but did not seem to cover the defects of the Pd surface. The Tamman temperature of Pt (747.4°C) is higher than Pd (641°C). Therefore, for the case of Pd/Pt membranes, Pt was in a state of lower molecular mobility than Pd and consequently at the Pt-Pd boundary, the Kirkendall effect took place. Pd crossed the Pt-Pd boundary and diffused into the Pt layer; while Pt remained relatively stationary. This effect seemed to generate defects on the Pd layer.

In the case of Pd/Au/Pt, Au has the highest mobility and can diffuse towards the Au-Pd or Au-Pt. Nevertheless, since the Tamman temperature of Pd is lower than Pt, Au will have a tendency to diffuse towards Pd. That was the reason why the curing effects of Au were notable in the ternary alloy. The diffusion of Pd towards Pt was minimized due to the presence of Au between both metals.

5. Conclusions

The effective performance of different Pd and Pd/Alloy composite asymmetric membranes under coal-derived syngas at a pilot scale was comparatively assessed. The present research study offers important insights on these membranes in industrial settings by clearly identifying and illustrating their respective strengths and weaknesses which can be condensed as follows:

- Palladium and Pd/Alloy membranes are susceptible to sulfur poisoning at even small quantities mainly resulting in a reduction in H₂ permeances.
- The robustness of Pd membranes under industrial settings significantly increases with the existence of an alloy such as Au and/or Pt.
- The use of Pt as a sulfur resistant alloy showed promising preliminary results, but requires further investigation.
- Ternary composite membranes under industrial settings were successfully demonstrated displaying high H₂ permeance, good H₂ quality and robustness of operation. *To the best of our knowledge, this is the first time the results of a performance assessment of Pd/Au/Pt membranes are reported in the pertinent literature.*
- It was suspected that Au is responsible for the protection of the membrane, acting as a patch paste blocking any defects at the surface of the Pd layer.

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References

- [1] Koros WJ, Mahajan R. Pushing the limits on possibilities for large scale gas separation: Which strategies? *J Membr Sci* 2000; 175: 181-196.
- [2] Koc R, Kazantzis NK, Ma YH. Membrane technology embedded into IGCC plants with CO₂ capture: An economic performance evaluation under uncertainty. *Int J Greenh. Gas Contr.* 2014; 26: 22–38.
- [3] Koc R, Kazantzis NK, Nuttall WJ, Ma YH. An economic evaluation framework for membrane reactors in the presence of uncertainty: The case for process safety investment and risk reduction. *J Loss Prev Proc. Ind* 2013; 26: 468-477.
- [4] Gryaznov VM. Hydrogen permeable palladium membrane catalysts: An aid to the efficient production of ultrapure chemicals and pharmaceuticals. *Platinum Metals Rev* 1986; 30: 68-72.
- [5] Gryaznov VM. Metal containing membranes for the production of ultrapure hydrogen and the recovery of hydrogen isotopes. *Separ Purif Method* 2000; 29(2): 171-187.
- [6] Guazzone F, Catalano J, Mardilovich IP, Knier J, Pande S, Wu T, Lambrecht RC, Datta S, Kazantzis NK, Ma YH. Gas permeation field tests of composite Pd and Pd-Au membranes in actual coal derived syngas atmosphere. *Int J Hydrogen Energy* 2012; 37: 14557-14568.
- [7] De Falco M, Iaquaniello G, Salladini A. Experimental tests on steam reforming of natural gas in a reformer and membrane modules (RMM) plant. *J Membr Sci* 2011; 368: 264-274.
- [8] Shirasaki Y, Tsuneki T, Ota Y, Yasuda I, Tachibana S, Nakajima H. Development of membrane reformer system for highly efficient hydrogen production from natural gas. *Int J Hydrogen Energy* 2009; 34, 4482-4487.
- [9] Catalano J, Guazzone F, Mardilovich IP, Kazantzis NK, Ma YH. Hydrogen production in a large scale water-gas shift Pd-based catalytic membrane reactor. *Ind Eng Chem Res* 2013; 52: 1042-1055.
- [10] Pomerantz N, Ma YH. Novel method for producing high H₂ permeability Pd membranes with a thin layer of the sulfur tolerant Pd/Cu fcc phase. *J Membr Sci* 2011; 370: 97–108.
- [11] Sonwane CG, Wilcox J, Ma YH. Achieving optimum hydrogen permeability in PdAg and PdAu alloys. *J Chem Phys* 2006; 125: 1-10.

-
- [12] Ma YH, Chen CH, Catalano J, Guazzone F, Payzant EA. Synthesis, annealing and performances of Pd-Au asymmetric composite membranes for hydrogen purification. *Ind Eng Chem Res* 2013; 52: 8732-8744.
- [13] Chen C, Ma YH. The effect of H₂S on the performance of Pd and Pd/Au composite membrane. *J Membr Sci* 2010; 362: 535-544.
- [14] Guazzone F, Catalano J, Mardilovich IP, Wu T, Lambrecht RC, Datta S, Knier J, Pande S, Kazantzis NK, Ma YH. Enhancement of the long-term permeance, selectivity stability, and recoverability of Pd-Au membranes in coal derived syngas atmospheres. *Energy Fuels* 2013; 27: 4150-4160.
- [15] Augustine AS, Mardilovich IP, Kazantzis NK, Ma YH. Durability of PSS-supported Pd-membranes under mixed gas and water–gas shift conditions. *J Membr Sci* 2012; 415-146: 213-220.
- [16] Ma YH, Mardilovich PP, She Y. (2000) Hydrogen gas-extraction module and method fabrication. US Patent No. 6,152,987.
- [17] Ma YH, Mardilovich IP, Engwall EE. (2007) Composite gas separation modules having intermediate metal layer. US Patent No. 7,175,694.
- [18] Ma YH, Guazzone F. (2010) Method for fabricating a composite gas separation module. US Patent No. 7,727,596.
- [19] Ma YH, Mardilovich IP, Engwall EE. (2008) Method for fabricating composite gas separation modules. US Patent No. 7,390,536.
- [20] Ma YH, Mardilovich IP, Engwall EE. (2007) Method for curing defects in the fabrication of a composite gas separation module. US Patent No. 7,172,644.
- [21] Ma YH, Mardilovich IP, Engwall EE. Thin composite palladium and palladium/alloy membranes for hydrogen separation. *Ann NY Acad Sci* 2003; 984: 346-360.
- [22] Ma YH, Mardilovich IP, Engwall EE. (2007) Composite gas separation modules having high Tamman temperature intermediate layers. US Patent No. 7,255,726.
- [23] McKinley DL. (1967) Metal alloy for hydrogen separation and purification. US Patent No. 3,350,845.
- [24] Southern company services Inc., Power systems development facility (PSDF) final report, DOE Cooperative Agreement, DE-FC21-90MC25140, April 2009 p. 1-158.
- [25] Yun S, Oyama ST. Correlations in palladium membranes for hydrogen separation: A review. *J Membr Sci* 2011; 375: 28-45.
- [26] Guo Y, Hongye Zou, Wu H, Zhou L, Liu H, Zhang X. Preparation of palladium membrane by bio-membrane assisted electroless plating for hydrogen separation. *Int J Hydrogen Energy* 2014; 39: 7069–7076.

-
- [27] Zhang K, Gao H, Rui Z, Liu P, Li Y, Lin YS. High-temperature stability of palladium membranes on porous metal supports with different intermediate layers. *Ind Eng Chem Res* 2009; 48: 1880–1886.
- [28] Ryi SK, Lee SW, Oh DK, Seo BS, Park JW, Park JS, Lee DW, Kim SS. Electroless plating of Pd after shielding the bottom of planar porous stainless steel for a highly stable hydrogen selective membrane. *J Membr Sci* 2014; 467: 93–99.
- [29] Berseneva FN, Timofeev NI, Zakharov AB. Alloys of palladium with metals of the platinum group as hydrogen-permeable membrane components at high temperatures of gas separation. *Int. J Hydrogen Energy* 1993; 19: 15-18.
- [30] Noh H, Flanagan TB, Sonoda T, Sakamoto Y. Solubility and thermodynamics of hydrogen in homogeneous f.c.c. Pd-Pt alloys. *J Alloys Compd* 1995; 228: 164-171.
- [31] Vigier F, Jurczakowski R, Lasia A. Determination of hydrogen absorption isotherm and diffusion coefficient in Pd₈Pt₁₉ alloy. *J Electroanal Chem* 2006; 588: 32-43.
- [32] Kajiwaru M, Uemiya S, Kojima T. Stability and hydrogen permeation behavior of supported platinum membranes in presence of hydrogen sulfide. *Int J Hydrogen Energy* 1999; 24: 839-844.
- [33] Kim DW, Park YJ, Moon JW, Ryi SK, Park JS. The effect of Cu reflow on the Pd-Cu-Ni ternary alloy membrane fabrication for Infinite hydrogen separation. *Thin Solid Films* 2008; 516: 3036-3044.
- [34] Tarditi AM, Cornaglia LM. Novel PdAgCu ternary alloy as promising materials for hydrogen separation membranes: Synthesis and characterization. *Surf Sci* 2011; 605: 62-71.
- [35] Coulter KE, Way JD, Gade SK, Chaudhari S, Sholl DS, Semidey-Flecha L. Predicting, fabricating and permeability testing of free-standing ternary palladium-copper-gold membranes for hydrogen separation. *J Phys Chem C* 2010; 114: 17173-17180.
- [36] Kirkendall EO. Diffusion of zinc in alpha brass. *Trans AIME* 1942; 147: 104-110.