Rapid annealing of sequentially plated Pd-Au composite membranes using high pressure hydrogen

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ABSTRACT

In this work, the time-consuming process of annealing Pd-Au alloy composite membranes, fabricated by sequential electroless plating, has been revisited. Composite Pd-Au/YSZ membranes approximately 5 μm thick with compositions ranging from 8 wt% to 10 wt% Au were fabricated by the bi-layer fabrication technique. Using these membranes, we investigated the effect of changing the pressure of the annealing gas (H_2) on annealing time at temperatures between 450 $^{\circ}\text{C}$ and 550 $^{\circ}\text{C}$. X-ray diffraction (XRD) was used to study the progress of annealing, where it was observed that a ~ 10 wt% Au membrane could be annealed in 9 h at 550 $^{\circ}\text{C}$ and 3 MPa H_2 whereas it took 120 h to anneal a similar membrane at 550 $^{\circ}\text{C}$ and 0.1 MPa H_2 . Another ~ 10 wt% Au membrane was annealed in less than 2 days at 450 $^{\circ}\text{C}$ and 3 MPa H_2 . Complete annealing was confirmed using energy dispersive x-ray spectroscopy (EDS) with multiple spot scans throughout the thickness of the membrane indicating a uniform Au composition. Additionally, it was found that the apparent activation energy for hydrogen permeation (E_{act}) could be used as an in situ parameter to judge the extent of annealing. In this technique, apparent E_{act} decreases as the membrane anneals, reaching a minimum value which is characteristic of its Au composition. Additional annealing time does not further change the apparent E_{act} for a membrane with a homogeneous Au distribution.

Keywords:

PdAu membrane

PdAu alloy formation

High pressure hydrogen

Apparent activation energy of hydrogen permeation

Electroless plating/deposition

1 Introduction

Hydrogen is not an energy source but rather an energy carrier (i.e. a secondary form of energy like electricity) which must be generated [1]. Among the varied uses of hydrogen, it is

predominantly used as a reactant in hydroprocessing of petroleum and in the manufacture of synthetic fertilizers, but can also be used as a fuel in proton-exchange membrane fuel cells [2,3]. The primary methods used to generate hydrogen (in the form of syngas) include coal gasification, methane steam reforming and catalytic partial oxidation [2]. However, hydrogen is only one component of syngas, which also contains CO, CO₂, steam, methane, sulfides and higher hydrocarbons [4,5], making purification necessary.

Pd-based membranes have been acknowledged as an alternative to separate and purify hydrogen because of their ability to produce ultra-pure hydrogen with high throughput and recovery [5–7]. The separator modules are more compact and contain fewer moving parts than other separation techniques [5]. Because sulfur poisoning of pure Pd membranes causes a loss in purity as well as throughput and recovery, Pd can be alloyed with Au to improve the sulfur tolerance of the membranes [4,8–13].

The as-prepared membranes need to be alloyed/annealed before they can be used to separate and purify hydrogen. Annealing thick (c.a. 10 μm) bi-layer Pd-Au membranes took more than 4 days at 500 °C [9]. Although annealing at a higher temperature (550 °C) for 1 day achieved a similar extent of annealing, the membrane still had a concentration gradient through its thickness [9]. Bi-layer membranes of similar thicknesses needed to be heated to 750 °C in order to bring the annealing time down to 20 h [13]. Thinner membranes (c.a. 4 μm to 6 μm) annealed at 500 °C for 5 days [14], in addition to a 5 day pre-anneal at the same temperature, showed enrichment in Au in the top couple of microns [11]. 3 μm to 5 μm thick membranes treated at 600 °C needed to be annealed for a week at that temperature in order to form a homogeneous alloy [15]. Thus, there is a need to reduce the annealing time to enable fast and simple fabrication of Pd-Au alloy composite membranes.

One possible solution was to fabricate a membrane with multiple alternating nanolayers of Pd and Au, which was studied by Shi et al. (2011). They found that a membrane fabricated via alternating nanolayers could be annealed in less than a week at 500 °C [16]. However, this can still be considered a lengthy period of time, not to mention the complex and time-consuming nature of the fabrication process. Another solution was to increase the annealing temperature, which was shown to be effective by Gade et al. (2009) when they annealed 9 μm to 10 μm thick membranes at 750 °C [13]. The issue is that such temperatures (750 °C), which are above the Tammann temperature of both Pd and Au, can be detrimental to the performance of thinner membranes [13]. Even temperatures as low as 550 °C were found to cause a decline in the integrity, and thus selectivity, of a thin membrane (c.a. 5 μm) when it was exposed to that temperature for close to two weeks [15].

Extended exposure of composite membranes to temperatures of 500 °C and above results in rearrangement of the film, and formation and growth of grains; these two effects are termed as annealing of the film and sintering, respectively [17]. Surface smoothening (a consequence of sintering of the surface) leads to the reduction in the surface area for hydrogen dissociation [17]

and possibly also a reduction in the absorption rate of hydrogen into the film [18]. Bulk rearrangement of the film, which might include annealing out micro-cracks and reducing the concentration of grain boundaries - both of which are thought to be avenues for hydrogen permeation, causes a decrease in the hydrogen flux [17]. Another consequence of the high temperature testing of composite membranes is the increase in the nitrogen flux. This increase is attributed to the increased porosity of the film due to the formation of pinholes or micro-channels in the film resulting from the annealing process [17]. Thus, the challenge is to reduce the annealing time while limiting the increase in the annealing temperature.

All of the previous annealing studies on Pd-Au were conducted either under N₂ [13] or atmospheric H₂ [9,11,14–16,19]. As for evidence that high hydrogen pressure may assist in the annealing process, Flanagan and Noh (1995) found that hydrogen heat treatment (HHT) on Pd-Ni alloys (c.a. 100 µm) at elevated temperatures (550 °C) and 5.5 MPa for 4 h resulted in elimination of the compositional variations in an initially inhomogeneous alloy [20]. Similar results were seen on HHT of initially inhomogeneous Pd-Pt alloys at 400 °C and 30.0 MPa for 12.7 h [21,22].

Finally, post-testing analysis techniques such as x-ray diffraction (XRD) and cross-sectional scanning electron microscopy (SEM) coupled with energy dispersive x-ray spectroscopy (EDS) as the only tools to determine the extent of annealing are inconvenient and time-consuming because the membrane has to be cooled to room temperature and removed from the testing module before it can be analyzed; not to mention the destructive nature of both these techniques. Thus, an in situ parameter to judge the extent of annealing would be extremely useful. The apparent activation energy for hydrogen permeation (E_{act}) for a cold-rolled Pd-Ag foil of a given Ag composition can be easily computed and these values are available in the literature [23]. Based on the Ag composition of a Pd-Ag composite membrane and a cold-rolled foil of similar Ag composition, it was shown that the apparent E_{act} can be used as an in situ parameter to judge the extent of annealing for sequentially plated bi-layer Pd-Ag composite membranes [23]. It was also shown that once a Pd-Ag membrane was annealed there was no further change in the apparent E_{act} .

In this work, the effect of hydrogen pressure on annealing time was studied. An as-fabricated Pd-Au bi-layer can be viewed as an extreme case of an inhomogeneous alloy in which there is one region of pure Au (or low Pd) and another region of pure Pd (or high Pd). For this study the highest hydrogen pressure investigated was 3.0 MPa, due to equipment limitations, and the highest annealing temperature was 550 °C. A recent study showed that annealing under permeating versus non-permeating hydrogen did not affect the alloying process [14]. Thus, the annealing experiments were conducted in non-permeating mode to reduce hydrogen gas consumption. In addition, the hypothesis that apparent E_{act} can be used as an in situ parameter to judge the extent of annealing for composite Pd-Au alloy membranes was also investigated. It is considered that the apparent E_{act} could be a valuable in situ analysis tool to judge the extent of annealing without the need for ex situ, and most commonly destructive, analyses. Analysis

techniques including XRD and cross-sectional SEM/EDS were used to verify that the membrane was annealed and thus supports the aforementioned hypothesis.

2 Experimental

2.1 Substrates, their cleaning and characterization

Porous, asymmetric, tubular yttria-stabilized zirconia (YSZ) substrates were obtained from our industrial collaborators at Praxair Surface Technologies, IN. The substrates were received as 20 cm long pieces with an outer diameter of 1 cm but can then be cut to any desired length. For this study, each substrate was cut into two 10 cm long pieces and cleaned as described previously by Hawa et al. (2014) [24]. Finally, every piece was mounted and characterized by flow porometry to ensure consistent pore sizes. The size of the largest pore in the top layer of the substrate was obtained from the first bubble point (FBP) measurement as defined by the ASTM F-316-03 standard [25].

2.2 Membrane synthesis

Pd-Au alloy composite membranes described in this work were fabricated by sequential electroless plating (ELP) followed by annealing to obtain a homogeneous alloy. The activation, reduction, Pd and Au plating bath recipes are given in Table 1 [11,24,26,27]. First, the substrate must be activated because a layer of Pd nano-particles is required to serve as catalytic nucleation sites for the growth of the electroless film [17]. For activation, an air brush was used to spray the outside of the characterized substrate with a solution of palladium acetate in chloroform. The substrate was then calcined at 350 °C (which is above the decomposition temperature of palladium acetate [28]) for 5 h to give a layer of nanocrystalline palladium oxide on the surface. The palladium oxide was then reduced to metallic Pd in a basic dilute hydrazine solution (reduction solution) before the dense Pd layer was deposited by ELP.

All Pd-Au composite membranes fabricated for this study were plated sequentially, meaning that first Pd was deposited followed by Au using separate plating baths. For multi-layer fabrication, this layering scheme was repeated until the desired thickness and composition was achieved. Plating was conducted in a 100 mL graduated cylinder using a heated water bath when necessary (reduction and Au plating steps). The ratio of plated surface area to plating solution volume was maintained at 0.5 cm²/cm³.

For fast plating kinetics, as is the case with Pd, the bubbles generated as a by-product of the plating reaction can potentially adhere to the surface leading to micro-porosities in the film. This micro-porosity has been suggested as a cause of leak growth once the film is heated to the operating temperature [6,29]. To alleviate this issue, the graduated cylinder was placed in an ultrasonic water bath to dislodge bubbles during the Pd plating cycles.

The Au plating mechanism, on the other hand, does not require a reducing agent due to a displacement plating mechanism. Because Au has a more positive reduction potential than Pd,

Au can displace Pd in the film, meaning that the Au plating reaction proceeds well on a Pd surface but is self-limiting and stops when a dense layer of surface Au is formed [13]. It was observed here that the Au plating thickness was limited to between 0.2 μm and 0.3 μm .

Table 1

Bath recipes for activation, reduction, Pd and Au.

Component	Activation	Reduction	Pd	Au
Palladium (II) acetate, 99% pure	35 g/L			
Chloroform, HPLC grade	1000 mL/L			
Deionized water		599 mL/L	599 mL/L	1000 mL/L
Ammonium hydroxide, 28-30 wt%		390 mL/L	390 mL/L	
Palladium (II) chloride, 99% pure			2.7 g/L	
Hydrazine, 1 M		10 mL/L	10 mL/L	
Sodium hydroxide				10 g/L
Gold (III) chloride, 99% pure				1 g/L
Temperature		55 °C	20 °C	55 °C
Plating time			2 h	20 h
Plating thickness			1 μm	0.3 μm

2.3 Membrane testing

Membranes with a low leak at room temperature (N_2 permeance $\leq 1.0\text{E-}09 \text{ mol/m}^2/\text{s/Pa}$) were mounted in Swagelok stainless steel compression fittings using graphite ferrules obtained from Chromtech, Australia. The mounted membrane was then installed in a stainless steel cylindrical test housing (shell-and-tube configuration) and placed in a Lindberg MiniMite tube furnace. The test housing and setup have been described previously [13,24]. The membranes were heated and cooled at a rate of 3 °C/min under flowing N_2 . At temperatures below 300 °C, palladium undergoes a phase transition in the presence of hydrogen, which results in a larger lattice size as it absorbs hydrogen, ultimately causing warping and embrittlement of the film [6,30]. To avoid this, the atmosphere was changed to hydrogen only when the permeate stream temperature exceeded 350 °C.

Permeation tests were conducted with industrial grade hydrogen ($\geq 99.90\%$ purity) and industrial grade nitrogen ($\geq 99.00\%$ purity), which were fed to the membrane one gas at a time on the shell side. The feed pressure to the membrane was controlled with a back-pressure regulator on the retentate stream. The pressure drop from the feed to the retentate was negligible and the retentate flow was maintained at a minimum. The permeate stream exited on the tube side at atmospheric pressure, which was about 83 kPa. The permeate stream flow rate was measured with a digital bubble flow meter. The membrane was cycled in temperature (350 °C – 550 °C) as well as pressure (138 kPa – 690 kPa) to calculate H_2 permeance as function of temperature which was used to calculate the apparent E_{act} .

2.4 Membrane characterization

The composition and thickness of the Pd-Au alloy composite membranes were obtained from gravimetric measurements (GM) and x-ray fluorescence (XRF) analysis. Post-annealing analysis tools include inductively coupled plasma-atomic emission spectroscopy (ICP-AES), scanning electron microscopy (SEM) coupled with energy dispersive x-ray spectroscopy (EDS), and x-ray diffraction (XRD). A brief description of each analysis technique is given below. In order to remove the film from the substrate, it was exposed to 690 kPa H₂ at room temperature followed by exposure to air. Such treatment causes hydrogen embrittlement of the film [6].

2.4.1 X-Ray fluorescence (XRF)

Fischerscope XDLM-C4 PCB spectrometer was used to measure the thickness as well as the bulk composition of the Pd-Au alloy composite membranes. A Ni filter with an accelerating voltage of 50.0 keV was used. Multiple line scans were conducted along the length of the membrane to obtain an average thickness and bulk composition. The sampling depth (R_{KO} , μm) depends on initial beam energy (E_0 , keV), and atomic weight (A , g/mol), atomic number (Z) and density (ρ , g/cm³) of the sample; as given by the Kanaya-Okayama range equation (Equation 1) [31]. At 50.0 keV, the sampling depth in Pd is estimated to be 5.6 μm , which is greater than the thickness of membranes used in this study. Thus, XRF can be considered as a bulk analysis technique for the purposes of this study.

$$R_{KO} = \frac{0.0276 \cdot A \cdot E_0^{1.67}}{Z^{0.889} \cdot \rho} \quad \text{Equation 1}$$

2.4.2 Scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDS)

JEOL JSM-7000F FESEM was used to image the cross section of the membranes. The Pd-Au alloy membrane was imaged after it was removed from the ceramic substrate in order to prevent charging of the sample. EDS scans were conducted at 25.0 keV to study the extent of annealing by analyzing the Au composition throughout the thickness of the membrane in addition to providing another estimate of the bulk Au composition. Using Equation 1 the sampling depth in Pd at 25.0 keV is estimated to be 1.8 μm .

2.4.3 X-Ray diffraction (XRD)

XRD was used to study the extent of annealing and to provide another estimate of the Au composition using Vegard's law [13,32,33]. XRD analysis on the annealed Pd-Au alloy composite membranes was performed using a Siemens Kristalloflex 810 instrument. X-rays were produced from a copper source at 25.0 mA and 30.0 keV. Scans were restricted to the relevant sections with a step size of 0.02° and a collection time of 3 seconds. The length of the sample was restricted to ≤ 5 cm due to equipment limitations. In most cases the samples were analyzed with the film still adhered to the tubular ceramic substrate. In one case the film was removed from the substrate in order to analyze the bottom side of the membrane. The peaks were analyzed using the Jade 9 software from MDI.

Liu et al (2010) derived an equation to calculate the effective penetration depth, z , in XRD (Equation 2), where N is the noise, S_0 is the detected signal, μ is the linear absorption coefficient (product of the density ρ and the mass attenuation coefficient μ/ρ [34]), Ω is the incident angle and $2\theta - \Omega$ is the diffracted angle [35]. The x-ray attenuation length is defined as the depth into the material along the surface normal where the intensity of the x-rays falls to $1/e$ of its value at the surface (e is the base of the natural log). Hence, using $N/S_0 + N = 1/e$ and $\Omega = \theta$, Equation 2 reduces to Equation 3. At 30.0 keV $\mu_{Pd} = 416.6 \text{ cm}^{-1}$, and for the Pd-111 peak $2\theta = 40.12^\circ$; using those values in Equation 3 gives $z = 4.1 \text{ }\mu\text{m}$. For Pd-311 peak $2\theta = 82.1^\circ$ and $z = 7.9 \text{ }\mu\text{m}$. For a 10 wt% Au in Pd alloy, μ can be calculated from Equation 4 and Equation 5. Using that value of μ in Equation 3 gives $z = 4.0 \text{ }\mu\text{m}$. On account of the low Au content in the alloy the value of z is essentially unchanged and >80% of thickness of the film is sampled even by the lowest Pd peak.

$$z = \frac{\ln(N/(S_0 + N))}{-\mu(1/\sin(\Omega) + 1/\sin(2\theta - \Omega))} \quad \text{Equation 2}$$

$$z = \frac{\sin(\theta)}{2\mu} \quad \text{Equation 3}$$

$$\left(\frac{\mu}{\rho}\right) = \sum_i w_i \left(\frac{\mu}{\rho}\right)_i \quad \text{Equation 4}$$

$$\left(\frac{1}{\rho}\right) = \sum_i \frac{w_i}{\rho_i} \quad \text{Equation 5}$$

2.4.4 Inductively coupled plasma – atomic emission spectroscopy (ICP-AES)

ICP-AES was used to confirm the composition obtained from the other analysis techniques (GM, XRF, XRD and EDS). A small piece of the Pd-Au alloy membrane was dissolved in aqua regia until there were no solids observed in the solution. The total dissolved solids (TDS) were less than 0.01% and the pH of the solution was adjusted to be about 1. ICP-AES was performed using a Perkin Elmer Optima 5300 DV instrument in Prof. James Ranville's laboratory in the chemistry department at the Colorado School of Mines (Golden, Colorado).

3 Results and discussion

3.1 XRD on tubular substrate

In order to verify whether XRD analysis could be conducted on a film while it was still adhered to the substrate, a 3.1 μm pure Pd membrane (9061-4A-2) was analyzed by XRD while the film was still adhered to the tubular substrate. This membrane was tested for more than 100 h at 400 $^\circ\text{C}$ following which XRD analysis was conducted. From Fig. 1 it can be seen that the location of the Pd 111 peak is at $2\theta = 40.12^\circ$ which is consistent with the value reported in the ICDD database (Pd: card 46-1043, Au: card 04-0784).

Fig. 1. XRD pattern for membrane 9061-4A-2. This was a 3.1 μm pure Pd membrane.

3.2 High pressure annealing

3.2.1 Membrane synthesis

The bi-layer fabrication strategy is simple and fast, hence it may be preferred for large scale fabrication of membranes in the industry. Three 10 cm membranes, between 4 μm and 5 μm thick ranging from 8 wt% to 10 wt % Au, were fabricated as bi-layers for this study. After fabrication, they were cut into 2 cm pieces to study the progress of annealing using XRD. The details of those membranes are given in Table 2. The compositions calculated or measured from the different analysis techniques were consistent. The thickness estimate from SEM was slightly lower than that obtained from GM and XRF which is discussed below in section 3.2.2.

Table 2

Summary of membranes synthesized for high hydrogen pressure annealing study.

Membrane ID	Composition (Au wt%)				Thickness (μm)		
	GM	XRF	XRD	EDS	GM	XRF	SEM
9093-19B	8.9	9.5	8.8	8.0	4.8	4.9 ± 0.3	4.3 ± 0.5
9081-5A-1	8.8	8.3	8.9	-	4.8	4.8 ± 0.3	-
9081-5A-2	9.0	8.5	9.0	-	4.8	4.9 ± 0.3	-

3.2.2 Annealing study

A piece of 9093-19B was annealed at 550 °C and 3.0 MPa H₂. XRD analysis was conducted while the film was still adhered to the tubular substrate. The evolution of the XRD pattern for the 111 peak is shown in Fig. 2. Before any annealing, the 111 peaks for both Au and Pd were clearly visible. Within the first 30 minutes of annealing, the pure Au 111 peak had disappeared and a shoulder had appeared on the slightly shifted Pd 111 peak. This suggests that there were two regions within the membrane having two different Au compositions.

Fig. 2. Evolution of the XRD pattern of the 111 peak for an 8.8 wt% Au sample from membrane 9093-19B annealed at 550 °C and 3.0 MPa H₂.

On further annealing, the shoulder was assimilated into the primary Pd-Au 111 peak after about 360 minutes. Additional annealing moved the Pd-Au 111 peak closer to the Pd 111 peak. The Au composition was estimated from the Pd-Au alloy peaks using Vegard's law [13,32,33]. The final Au composition was calculated to be 8.8 ± 2.8 wt% Au (lattice constant = 3.8990 Å) which is in good agreement with XRF and GM estimates. This estimate was obtained by averaging the compositions calculated for the 111, 200, 220, and 311 peaks, while the error was calculated using the student's t-distribution with a confidence interval of 95%.

In order to verify that a uniform alloy had been formed, another piece of the same membrane (9093-19B) was annealed at the same conditions. The film from that piece was then removed from the substrate to facilitate analysis of both the top and bottom surface of the annealed film. Compositions from the XRD patterns of the top and bottom surface of the

membrane agreed with each other, with the Au composition being calculated as 8.1 wt% (lattice constant = 3.8982 Å) for the top surface and 8.0 wt% (lattice constant = 3.8981 Å) for the bottom surface. This result is in good agreement with the composition measured by GM, XRF and EDS, further suggesting complete alloying of the bi-layer film (Fig. 3).

Fig. 3. Top and bottom surface XRD pattern of the 111 peak for the 8.8 wt% Au piece annealed at 550 °C and 3.0 MPa H₂.

The cross-section of a piece of the removed film was analyzed with SEM (Fig. 4). Using five measurements (not shown) the thickness was estimated to be 4.3 ± 0.5 μm. On activating the substrate, some of the Pd seed layer penetrates into the pores of the support. This porous layer remains in the support upon delamination of the film which could explain the difference in the thickness estimates in Table 2. Within an 8% error, the estimates from GM, XRF, and SEM are equal. EDS analysis was also performed by doing spot scans throughout the thickness of the membrane. It was shown that the Au composition was very uniform throughout the thickness and agreed well with the other techniques used to estimate the composition of Au in the film. The results of the EDS line scan analysis are shown in Fig. 4.

Fig. 4. SEM image and EDS of the cross-section of the film removed from the 8.8 wt% Au piece which was annealed at 550 °C and 3.0 MPa H₂. The dashed line represents the average Au composition while the arrow points towards the ceramic substrate-film interface side.

Similar to the sample just described, several other samples were exposed to a variety of temperatures and pressures. For each, the required time to anneal the film is given in Table 3. The slowest three conditions, marked with an 'x', are not included because the annealing time was estimated to be greater than 400 h, which would simply be impractical to consider. The following indications were used to identify complete alloying:

1. Formation of single and symmetrical Pd-Au alloy peaks for the 111, 200, 220 and 311 peaks.
2. Agreement of average Au composition from XRD with XRF and GM.

3. Lack of movement of peaks upon additional annealing. This is also evidenced by no change in the average Au composition calculated using Vegard's law for all four peaks.

Table 3

Summary of the annealing times for approximately 9 wt% Au samples at each annealing condition studied.

	Annealing time (h)		
	550 °C	500 °C	450 °C
3.0 MPa H ₂	8.5	18	36
1.5 MPa H ₂	18	72	336
0.1 MPa H ₂	120	>400	☒
Industrial N ₂	216	☒	☒

3.2.3 Hypothesis for expedited annealing under high hydrogen pressure

H species are known to occupy octahedral sites in the Pd-Au fcc lattice [36]. The incorporation of hydrogen into the fcc lattice increases the lattice spacing as evidenced by a 20 pm increase in the lattice spacing for both Pd_{0.495}Au_{0.005}H_{0.500} and Pd_{0.48}Au_{0.05}H_{0.47} samples which were exposed to $p_{H_2} = 7.2$ GPa for 24 h at 325 °C [37,38]. It then follows that one hypothesis for the observed reduction in annealing times at higher H₂ pressures is that the expanded lattice facilitates solid state diffusion.

The hydrogen content, r , is expressed as a ratio of hydrogen atoms to the metal atoms present in the lattice and can be calculated from Equation 6 [39], where p_{H_2} is the hydrogen pressure in bar and a , b are constants that depend on the Au composition (Table 4) [37]. Similar values of r were obtained irrespective of the choice of the values for a , b .

Table 4

Summary of the values of a , b used for calculating r .

Alloy	T (°C)	$a \cdot 10^2$ [bar ^{-1/2}]	$b \cdot 10^2$ [bar]
Pd	427	1.02	0.068
Pd _{0.9} Au _{0.1}	427	1.16	0.041

Once r is known the lattice constant can be interpolated from graphs relating hydrogen content to the lattice constant [40]. At $p_{H_2} = 3.0$ MPa, $r \approx 7$ -8 at% and the relative change in the lattice constant was only 3 pm. Such a small change in lattice constant alone could not explain the drastically short annealing times.

$$r = \frac{H}{Pd + Au} = a \cdot \sqrt{p_{H_2}} + b \cdot p_{H_2} \quad \text{Equation 6}$$

Fukai and Ōkuma (1993) found that exposure of Ni and Pd to high pressure H₂ caused copious vacancy formation in the crystal lattice [41]. The concentration of the vacancies in the Pd-H system was found to be as high as 18 ± 3 at% at 5 GPa [42]. Based on those findings, and their own results, Flanagan and Noh (1995, 1996) hypothesized that the dissolved hydrogen catalyzed the metal atom diffusion by way of increases in the vacancy concentration of the lattice [20,21].

Pd and Au form a substitutional fcc solid solution which is continuous over the entire composition range [33,43]. The annealing process involves the inter-diffusion of the Pd and Au layers to form a homogeneous Pd-Au alloy, but the diffusivity of Au in Pd is one to two orders of magnitude smaller than the diffusivity of Pd in Au [44]. Thus, one can infer that alloying takes place primarily due to the dilution of the Au layer by Pd.

Neglecting the diffusion of Au into Pd, the process of alloying can be described by the semi-infinite slab, transient diffusion model given by Equation 7 [45], where A stands for Pd and B stands for Au, D_{AB} is the diffusion coefficient, and t is the annealing time required for the concentration, C_A , at the end of the Au layer (i.e. at $x = \delta$, thickness of Au layer) to become equal to the bulk concentration. Concentration can be written in terms of the weight fraction, w , and density, ρ , as $C_A = w_A \cdot \rho_{AB}$ and $C_{A,S} = w_{A,S} \cdot \rho_A$. Equation 8 through Equation 12 were derived by the authors.

At $t = 0$, $C_A(x > 0, 0) = C_{A,0} = 0$ because it is a pure Au layer. At $x = 0$, $C_A(0, t) = C_{A,S} = \rho_A$ because $w_{A,S} = 1$ for a pure Pd layer. Thus, Equation 7 is simplified to Equation 8, where ρ_{AB} is the density of the alloy given by Equation 9. Combining Equation 8 and Equation 9, and after some algebraic manipulation, we get Equation 10.

$$\frac{C_A - C_{A,0}}{C_{A,S} - C_{A,0}} = 1 - \operatorname{erf}\left(\frac{x}{\sqrt{4D_{AB}t}}\right) \quad \text{Equation 7}$$

$$w_A \cdot \frac{\rho_{AB}}{\rho_A} = 1 - \operatorname{erf}\left(\frac{x}{\sqrt{4D_{AB}t}}\right) \quad \text{Equation 8}$$

$$\frac{1}{\rho_{AB}} = \frac{w_A}{\rho_A} + \frac{w_B}{\rho_B} \quad \text{Equation 9}$$

$$\frac{w_B \cdot \rho_A}{w_A \cdot \rho_B + w_B \rho_A} = \operatorname{erf}\left(\frac{x}{\sqrt{4D_{AB}t}}\right) \quad \text{Equation 10}$$

When $x = \delta$ Equation 10 can be rewritten as Equation 11. For $w_A = 0.9$, $w_B = 0.1$, $\rho_A = 12.0 \text{ g/cm}^3$ and $\rho_B = 19.3 \text{ g/cm}^3$, $z = 0.06$; which is obtained from the error function table. Thus, for known δ and D_{AB} the annealing time can be predicted from Equation 11, or conversely, for known δ and t the inter-diffusion coefficient can be calculated.

$$\frac{w_B \cdot \rho_A}{w_A \cdot \rho_B + w_B \rho_A} = \operatorname{erf}\left(\frac{\delta}{\sqrt{4D_{AB}t}}\right) = \operatorname{erf}(z) \quad \text{Equation 11}$$

$$z = \frac{\delta}{\sqrt{4D_{AB}t}} \quad \text{Equation 12}$$

The temperature dependence of the inter-diffusion coefficient is given by the Arrhenius relationship shown in Equation 13, where D_0 is the pre-exponential factor, Q is the activation energy for inter-diffusion, R is the universal gas constant and T is the absolute temperature [46]. For Pd diffusing into Au, $D_0 = 7.6 \cdot 10^{-6} \text{ m}^2/\text{s}$ and $Q = 195.1 \text{ kJ/mol}$ [46]. At $T = 550 \text{ }^\circ\text{C}$ (823 K) a membrane with a $0.2 \text{ }\mu\text{m}$ Au layer would take 267 h to anneal.

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad \text{Equation 13}$$

In order to check the applicability of this simple model and eliminate any catalytic effects due to hydrogen, a piece of the membrane 9081-5A-1 was annealed for 216 h (9 days) at $550 \text{ }^\circ\text{C}$ in industrial N_2 after which XRD analysis was performed. Single, symmetrical peaks were seen for the Pd-Au alloy 111, 200, 220 and 311 peaks, which yielded a composition of $8.9 \pm 1.1 \text{ wt\%}$ Au. The overestimation of annealing time by the model might be explained by the fact that the model neglects the contribution of Au diffusing into Pd to the alloying process.

Having determined that this approximate model produces reasonable estimates, the annealing time data in Table 3 were used to predict the inter-diffusion coefficients for the different annealing conditions. The plot of $\ln(D)$ versus $1/T$ was linear (Fig. 5), the slope of which was $-Q/R$. In this way the activation energy for inter-diffusion was calculated for annealing at 1.5 MPa H_2 and 3.0 MPa H_2 . Those results are shown in Fig. 6, with the activation energy for diffusion of Pd in Au included for comparison [46].

Fig. 5. Dependence of the inter-diffusion coefficient on temperature at different H₂ pressures.

Traditionally a catalyst is added to enhance the rate of a reaction, accomplishing this by reducing the activation energy barrier between reactants and products. Analogous to that, the dissolved hydrogen (c.a. 7-8 at% at $p_{H_2} = 3.0$ MPa) reduced the activation energy for inter-diffusion by more than half from the literature value. Even at 1.5 MPa H₂, enhancement of the inter-diffusion process by the catalytic activity of H₂ was still seen. Shu et al (1996) reported similar results for the Pd-Ag system [47]. They found that the activation energy of Pd-Ag inter-diffusion was reduced from 183 kJ/mol in the absence of hydrogen to 72 kJ/mol in the presence of hydrogen, in the temperature range of 500 – 800 °C [47].

A catalyst enhances the rates of both the forward as well as the reverse reaction - the reverse reaction here being the segregation of the Pd-Au alloy (i.e. changing from a homogeneous alloy to one with a Pd-rich and Pd-poor region). This was the observed result for the Pd-Ni and Pd-Pt systems [20–22]. For the Pd-Pt system, a homogeneous alloy treated with 100 MPa H₂ at 200 °C for 3 h resulted in a phase segregated, inhomogeneous alloy [21,22]. It then follows that for the Pd-Au system there may be a limit to how high the hydrogen pressure can be increased in order to reduce annealing time. In other words, increasing the hydrogen pressure beyond a certain point could lead to the formation of a phase segregated alloy, rather than increasing the rate at which the homogenous alloy is formed. However, a study similar to the one performed on the Pd-Pt system by Flanagan and Noh (1996) [21] needs to be performed for the Pd-Au system to determine if a similar result will occur.

It is not lost on the authors that the effect of annealing under high pressure on the absolute values of both hydrogen and non-hydrogen gas permeances, as well as their stability under operating conditions, needs to be investigated. This will be the focus of future work.

Fig. 6. Effect of H₂ pressure on the activation energy of inter-diffusion and its comparison to literature.

3.3 Apparent E_{act} as an *in situ* parameter to judge extent of annealing

Membrane 9061-3A-1 was fabricated with 3 layers of Pd alternating with 3 layers of Au. A summary of the apparent E_{act} for this membrane at different stages during annealing is shown in Table 5. It was initially annealed for 5 days at 500 °C, as suggested in the literature [9,14]. The calculated value of apparent E_{act} (17.4 ± 0.8 kJ/mol) was more than twice the value reported for a cold-rolled foil of similar Au composition (Table 5). This suggested that the membrane was not completely annealed. Additional evidence of incomplete annealing was observed using surface EDS scans which showed that the surface Au composition was almost twice that of the bulk.

The annealing temperature was raised to 550 °C and within two days the apparent E_{act} had decreased to 8.6 ± 0.8 kJ/mol. The membrane was then annealed for 9 additional days during which the apparent E_{act} remained unchanged, with the final value of the apparent E_{act} agreeing well with the literature [19]. The membrane was thus deemed annealed and subsequently analyzed by XRD and ICP-AES. The XRD pattern for membrane 9061-3A-1 is shown in Fig. 7,

and a summary of the bulk Au composition from the different analysis techniques is given in Table 6.

Table 5

Heat treatment and activation energies for membrane 9061-3A-1 and comparison to literature.

Membrane ID/ Composition	Fabrication technique	Apparent E_{act} (kJ/mol)	Temperature range (°C)	Heat treatment
15 wt% Au [19]	Cold-rolled	8.6 ± 0.1	>200	-
9061-3A-1 (15 wt% Au)	ELP	17.4 ± 0.8	400-600	5 days at 500 °C
		9.7 ± 0.1	350-550	+ 1 day at 550 °C
		8.6 ± 0.8	350-550	+ 1 day at 550 °C
		8.6 ± 0.1	350-550	+ 9 days at 550 °C

Fig. 7. XRD pattern for membrane 9061-3A-1 after annealing. The membrane was 3.1 μm thick and 15 wt% Au.

Table 6

Compositional analysis for membrane 9061-3A-1.

Membrane ID	Thickness (μm)	Au wt%				
		XRF	GM	Apparent E_{act}	ICP-AES	XRD
9061-3A-1	3.1	16	15	15	13	17

Experimental data for the apparent E_{act} of cold-rolled foils, which were homogenous in composition, was published by Gade et al. (2010) [19]. In this study, additional membranes in the composition range 0 wt% to 21 wt% Au were also annealed and their apparent E_{act} calculated at the end of annealing. As can be seen in Fig. 8, good agreement was seen between these data and the literature. The trend is nearly linear in the 0 wt% to 21 wt% Au range, as indicated by a linear line regression. Thus, one can predict the apparent E_{act} for Au compositions for which published data is unavailable and use that number to judge the extent of annealing.

Fig. 8. Comparison of the apparent E_{act} for Pd-Au alloy composite membranes from this study and Shi et al. (2011) [16] to the apparent E_{act} for cold-rolled foils in the literature (labeled points) [19].

4 Conclusions

Due to the rather lengthy annealing time required at temperatures below 550 °C, it was desired to reduce the annealing time required to synthesize a homogenous Pd-Au alloy composite membrane. We showed that it is possible to anneal a ~10 wt% Au membrane, fabricated as a bi-layer, at temperatures as low as 450 °C in less than 2 days simply by increasing the hydrogen pressure to 3.0 MPa. This is likely facilitated by the catalytic activity of the dissolved hydrogen due to formation of significant vacancies in the crystal lattice [20,21]. Thus, a fast and simple way of fabricating ~10 wt% Au membranes has been shown. Additionally, a

simple semi-infinite slab, transient diffusion model was used to quantify the effect of hydrogen gas pressure on the activation energy of inter-diffusion.

It was also shown that the apparent activation energy of H₂ permeation (E_{act}) can be used as an in situ parameter to judge the extent of annealing. Over the course of annealing, the apparent E_{act} decreases until it reaches a minimum, whereupon additional annealing does not change the apparent E_{act} of the annealed membrane. The final value of the apparent E_{act} for a given membrane was found to be characteristic of its Au composition.

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