Hydrogen purification with palladium and palladium alloys on porous stainless steel membranes

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Abstract: Hydrogen purification membranes have been prepared via a simultaneous electroless plating of Pd and Ag on a 0.5 μm media grade Porous Stainless Steel (PSS). Effects of the electroless bath temperature, composition, annealing time and temperature were studied while developing the Pd coating. Very low but measurable N_2 fluxes were seen, ranging from 0.010 to 0.020 cm^3/cm^2-min at temperatures varying from 300°C to 400°C. As no helium flux was observed, it appears that nitrogen diffused, albeit much more slowly, through the same interstitial sites that hydrogen did. H_2 permeances varying from $(1.9–3.1) \times 10^{-2}$ cm^3/cm^2-min-$Pa^{0.5}$ were recorded between temperatures from 350°C to 550°C. Sievert's Law was seen to hold true at all temperatures. Short term stability and reproducibility of the H_2 permeance were confirmed. The activation energy (E_d) for H_2 permeance in the Pd-Ag layer was calculated from the permeance data to be 9 ± 1 kJ/mol.

Keywords: hydrogen purification; palladium; membrane; Sievert's Law; Porous Stainless Steel.

Biographical notes: James R. Brenner is a Faculty in Chemical Engineering at Florida Tech since 1998, and has worked in H_2 storage, purification and sensing using metal hydride thin films on Porous Stainless Steel (PSS) and Templated Porous Carbon (TPC)/PSS composite supports. He has performed research projects on biodiagnostic chips, electronic noses, metallic nanoparticles, polymer foams for the space shuttle's external tanks, pillared clays and molybdenum sulfides and characterization of and development for upgrading of coal, heavy oil, and lignin feedstocks. He has also won three teaching awards including Student-Nominated Outstanding Professor of the Year for Florida Tech in 2006.

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1   Introduction

Lasher et al. (2002) have suggested that it would be feasible to ship hydrocarbon fuel to filling stations, followed by a series of three reactions to supply the resulting 99.999+% H_2 to vehicles at approximately \$2/kg. Simplifying this process to just a membrane reformation of gasoline to H_2, with the rejected impurities being combusted and/or sequestered, is the most economically reasonable route to H_2 use in vehicles. However, CO and sulphur-containing gases produced during H_2 generation from hydrocarbon fuels are poisons of a fuel cell's Pt anode (Bauman, 2002; Knapton, 1977; Narusawa et al., 2003; Peachey et al., 1996).

Because of hydrogen's small size and the ease by which it dissociates on Pd and several other late transition metals, only hydrogen can diffuse through the interstitial sites in the Pd lattice. Any impurities in the H_2 must diffuse either through pinhole pores or along grain boundaries in the membrane. Purities as high as 99.9999999% H_2 have been reported (Johnson-Matthey, 2004; Power and Energy, 2003). However, due to high cost and poor mechanical characteristics during the α to β phase transition, research has focused on methods of reducing the amount of Pd needed using Pd-coated porous substrates (Bryden and Ying, 1995; Grashoff et al., 1983; Makrides et al., 1965; Mardilovich et al., 1998; Yeung and Cheng, 1999), increasing the H_2 flux, decreasing the effect of H_2 embrittlement (i.e. Pd alloys; Buxbaum and Kinney, 1996; Buxbaum and Marker 1993), and/or eliminating Pd as a membrane component. The H_2 flux follows Sievert's Law, where J is the flux in cm^3/cm^2-min, k = permeance in cm^3/cm^2-min-$Pa^{0.5}$ and P is pressure in Pa:

$$J = k\left(\sqrt{P_{\text{retentate}}} - \sqrt{P_{\text{permeate}}}\right) \tag{1}$$

Cracking of the membrane layer due to the formation of pinholes is a function of both the operating conditions and the interactions between the support and the Pd membrane. Membrane cracking due to this lattice distortion is termed H_2 embrittlement. Pure Pd membranes should be operated in the α-phase region to minimise such embrittlement (Grashoff et al., 1983). A successful composite membrane may be achieved by the application of a thin Pd coating to a dense, highly permeable metal, such as Porous Stainless Steel (PSS); commercially available Pd foils are too expensive and have low H_2 fluxes. Pd-coated Ta membranes (Rothenberger and Buxbaum, 2002, 2003) of this type have been demonstrated as H_2 separation devices in disk (Buxbaum and Marker, 1993), tubular (Buxbaum and Kinney, 1996; Buxbaum and Marker, 1993) and foil (Moss et al., 1998; Peachey et al., 1996) form. Alloying Pd with metals like Cu, Ag, Ru, Pt and Ni has also been explored to reduce the H_2 embrittlement (Buxbaum and Kinney, 1996; Iliuta et al., 2003; Knapton, 1977; Moss et al., 1998; Peachey et al., 1996). Recent studies demonstrate the effectiveness of alloying Pd with Cu to improve sulphur tolerance (Iyoha and Enick, 2005; Ma et al., 2005; Rothenberger et al., 2004).

An alternative that can provide both mechanical strength and a thin separation layer for a high H_2 flux and reduced Pd cost are membranes consisting of a thin Pd film supported on a porous substrate, such as Vycor glass (Yeung and Cheng, 1999), ceramic (Mardilovich et al., 1998), stainless steel (Jun and Lee, 2000; Tosti et al., 2002), etc. Vycor glass (Yeung and Cheng, 1999) or ceramic (Tosti et al., 2002) supported Pd membranes are relatively difficult to assemble. One way to improve the membrane stability is to create an intermediate intermetallic diffusion barrier layer (such as an oxide

layer) that is stable under reducing atmospheres at high temperatures. An alternate way to improve membrane stability is to add alloying elements to the Pd such as Ag (Piper, 1966; Shu et al., 1993, 1996a; Uemiya et al., 1991a; Yeung and Cheng, 1999) or Ru (Gryaznov et al., 1993; Iliuta et al., 2003; McKinley, 1967). Alloying Pd not only suppresses H_2 embrittlement, but also increases permeability (Knapton, 1977; Moss et al., 1998; Peachey et al., 1996; Piper, 1966; Ward and Dao, 1999; Yeung and Cheng, 1999).

The thermal expansion coefficients (CTE's) for the metallic film and the substrate should be close enough for structural stability during thermal cycling. PSS substrates are advantageous in this aspect (Ma et al., 2005). Ceramic supports crack due to CTE mismatch during thermal cycling (Tosti et al., 2002). Also, intermetallic diffusion of elements from the substrate to the metallic film causes deterioration of the H_2 flux and selectivity (Gryaznov et al., 1993; Shu et al., 1996a), especially for PSS supports. The effect of synthesis method on long-term stability and selectivity of the membranes has been summarised by Shu et al. (1991) and Rothenberger et al. (2003; 2004) for Pd and its alloys on a variety of supports (Chen et al., 2003; Hou and Hughes, 2003; Jun and Lee, 1999; Kikuchi et al., 2002; Li et al., 1996; Moron et al., 2002; Nam and Lee, 2000; O'Brien et al., 2001; Pan et al., 2003; Shu et al., 1997; Yeung et al., 1999). A summary of the H_2 fluxes is in Table 1.

Table 1   Pd membrane performance

Reference	Year	Pd (μm)	T(K)	P_{H_2},ret (kPa)	k $(mol/m^2/s/Pa^{0.5})$	N_{H_2} $(mol/m^2/s)$
Yeung et al.	1999b	1.6	623	256	8.8×10^{-5}	2.8×10^{-2}
Shu et al.	1996b	2	573	105–120	1.0×10^{-3}	3.1×10^{-1}
Yan et al.	1994	2	773	100–200	5.0×10^{-6}	5.0×10^{-1}
Uemiya et al.	1991b	20	673	150–394	1.1×10^{-5}	7.3×10^{-2}
Ma et al.	2003	21.3	623	101–202	3.3×10^{-4}	1.0×10^{-1}
Lin et al.	1998	22	623	202–1515	1.1×10^{-4}	3.7×10^{-2}
Mardilovich et al.	1998	24	623	151–404	3.0×10^{-2}	9.8×10^{-2}
Tosti et al.	2000	50	623	200	2.1×10^{-4}	6.8×10^{-2}
Jarosch and Lasa	2001	156	1023	425–603	2.6×10^{-5}	8.4×10^{-3}

Note: $P_{H_2,permeate} = 101.3$ kPa, $P_{H_2,sweep} = 0$ kPa.

Among the variety of techniques useful for deposition of alloys, electroless plating has become the method of choice due to its uniform deposition on complex shapes and large substrate areas, the hardness and adhesion properties of the deposited film, and its use of relatively simple and inexpensive equipment (Kikuchi et al., 2002; Meenan et al., 1994; Shu et al., 1996b). Electroless deposition is based on the controlled, autocatalytic reduction of a dissolved metallic salt by reducing agents at a substrate interface. Although conceptually straightforward, support quality, surface activation methods, electroless plating procedures and bath chemistry influence membrane selectivity, permeability and Pd/Pd-alloy film stability. Electrolessly plated Pd-Ag membranes can be prepared either by a *coating and diffusion* of separate Pd and Ag layers, or by *simultaneous coplating* of Pd and Ag from the same plating bath, followed by an annealing process. After forming a series of alternating layers of Pd and Ag via the

coating process, the diffusion necessary to achieve a homogeneous composition involves annealing in H_2 at very high temperatures (800–900°C) for many hours (Shu et al., 1993, 1996a; Ward and Dao, 1999). Lower annealing temperatures result in a compositional gradient across the membrane (Shu et al., 1996a), which can lead to poorer mechanical stability and lower permeation rates. Moreover, the high temperature necessary for such diffusion would negatively impact the porosity of the stainless steel. Since the deposited Pd and Ag grains are in very close proximity, coplating allows for the formation of homogeneous alloys at much lower temperatures. The complex kinetics involved in the coplating bath solution of Pd-Ag and the sensitivity of the Pd-Ag film composition on the composition and temperature of the plating bath solution has been the primary focus of other investigators (Lin et al., 1998; Mardilovich et al., 1998; Shu et al., 1993, 1996a; Ward and Dao, 1999; Yeung and Cheng, 1999; Yeung et al., 1999). At fixed plating temperatures of 328 or 333 K and $[N_2H_4]$ = 10 mM, when the Ag concentration was ≥ 10 at.% in the plating solution, the crystallite diameter is governed by Ag deposition kinetics, and Pd agglomerates around the Ag (Yeung and Cheng, 1999). Heating at 500°C for 8 hr resulted in a bimetallic Pd-Ag alloy (Yeung and Cheng, 1999). In the experimental procedure that follows for Pd-Ag coating by simultaneous electroless plating, the following parameters were fixed: [Metal] = 10 mM, $[N_2H_4]$ = 10 mM, $[NH_4OH]$ = 3 M, pH = 10.4 and T = 60°C (Yeung and Cheng, 1999).

The primary goal of this work was to develop a H_2 purifier from a Pd/Ag membrane prepared via electroless deposition to produce fuel cell quality H_2 that is stable with respect to CO, H_2S and SO_2 (Athavale and Totlani, 1989; Hsu and Buxbaum, 1985). H_2 and N_2 fluxes across Pd and Pd alloy membranes deposited on PSS have been measured. The tasks for this project consisted of

1   Construction of a portable gas handling system. The system includes provision for either pure H_2 or simulated reformate gas mixture, temperature control, monitoring of feed and permeate flow rates, sampling of permeate and reject for analytical purposes and pressure control.

2   Permeation experiments on fabricated Pd and Pd-Ag membrane purifiers including:

   a   verification of impermeability of N_2

   b   Sievert's Law plot for non-H_2 gases

   c   Sievert's Law plot for H_2 gas

   d   measurement of permeance versus temperature for H_2 gas

   e   permeation H_2 versus N_2

   f H_2 permeance stability over a length of time

   g   permeation selectivity of H_2 versus N_2

   h   purification of H_2 from CO

   i   repeat of items c–h

   j   purification of H_2 from H_2S

   k   repeat of items c–j.

This paper focuses on items 2a–2g.

2 Experimental

2.1 Synthesis

The following procedure for deposition of Pd and Ag on PSS and Non-porous Stainless Steel (NPSS) by electroless plating was based on those described by Yeung and Cheng (1999) and Shu (1993). With the exception of those samples that are specifically referred to as being prepared by a coating and diffusion method (i.e. Pd, then Ag, then Pd, etc., followed by a 600°C annealing), all Pd alloy samples were prepared via codeposition.

1   0.5 μm grade ¼'' OD porous 316L stainless steel tube welded to PSS tubes on both ends were purchased from Mott Corporation.

2   Any surface contaminants were removed by cleaning the tube in an ultrasonic bath with 1 M KOH solution at 60°C for half an hour. This cleaning procedure was followed by sequentially rinsing the tube in DI water and isopropanol.

3   The tube was treated for 5 min. with HCl, then rinsed with distilled H_2O.

4   After loading the SS tube into the tube furnace and wrapping it with quartz wool, the reactor was leak tested with dry air, then purged with 30 sccm dry air at room temperature for 5 min, before ramping up to 600°C at 3°C/min. After a 4 hr calcination treatment at 600°C, the samples were cooled in flowing dry air to 25°C.

5   The oxidised tube was activated by immersing the tube in baths of acidic $SnCl_2$ (1 g/L) and acidic $Pd(NH_3)_4Cl_2 \cdot H_2O$ (0.15 g/L). The immersion treatments were repeated 4–10 times (depending upon the amount of activation required) for 5 min each, and then the activated tube was dried for 2 hr at 120°C. After immersion in $SnCl_2$, each SS tube was rinsed in DI water. Then, after immersion in $Pd(NH_3)_4Cl_2 \cdot H_2O$, each SS tube was rinsed with 0.01 M HCl and DI H_2O.

6   The activated tube was immersed in the following electroless bath compositions (Table 2) at room temperature, with constant amounts of $Na_2EDTA \cdot 2H_2O$ (40.1 g/L), 29% NH_4OH (200 mL/L) and 1 M N_2H_4 (10 mL/L), and a constant pH = 10.4. After depletion of each plating solution, a new solution was provided and the procedure was repeated after rinsing the membrane.

7   Then the plating solution and tube were placed in a water bath at 60°C. Each electroless plating bath solution was replaced with fresh solution after every 90 min, and each sample was plated 12 times. Between changing of plating bath solutions, each plated tube was rinsed in DI water for 2–5 min at 60°C. After 5 min of Pd predeposition, the Ag was added for the codeposition (Shu, 1993; Yeung and Cheng, 1999).

8   To obtain the final Pd-Ag alloy, the palladium-silver/PSS membrane was annealed in flowing hydrogen at 400°C for 4 hr and 500°C for 4 hr.

Samples were then characterised using Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and Atomic Force Microscopy (AFM).

Table 2   Electroless bath composition

	Bath 1 (only Pd)	Bath 2 (only Ag)	Bath 3 (75Pd–25Ag)
$Pd(NH_3)_4Cl_2·H_2O$, g/L	2.63	–	2.11
$AgNO_3$, g/L	–	1.69	0.34

## 2.2 Pd/Ag metal hydride hydrogen purifier and gas handling manifold

A schematic of a metal hydride H_2 purifier, and the completed gas handling manifold are shown in Figures 1 and 2, respectively. The outer tube of the purifier was a 316 SS 1-1/2 (3.81 cm) Schedule 40 6.08" (15.44 cm) long pipe with 0.31" (0.79 cm) thick end plugs on both sides. At the bottom left of Figure 2 were 0.5 μm grade 1/4" (0.635 cm) OD porous 316 stainless steel tubes welded to NPSS on both ends. At the bottom left are two 0.260" (0.660 cm) ID wells for ¼" (0.635 cm) OD, 5" (12.7 cm) long, 305 Watt electric cartridge heaters. A thermowell with a 0.192" (0.488 cm) ID housed a 3/16" (0.476 cm) OD 3-point K-type thermocouple that sensed temperature just past the entrance, in the middle, and just prior to the purifier exit. The entire purifier was surrounded with 2" (5.1 cm) thick quartz wool insulation. Permeation of H_2 and N_2 was measured at temperature ranges 573–823 K. Flow rates and pressures were measured using Unit Instruments mass flow controllers (0–50, 0–150 or 0–200 sccm) and Span Instruments 0–250 psia (17.2 MPa) pressure transducers and acquired using National Instruments LabView 7.0. Unit Instruments and Span Instruments are now part of Celerity, Inc. All temperatures were measured with either J-type or K-type 1/8" (0.318 cm) thermocouples from Omega Corporation. Temperature control was to $\pm$ 1°C using programmable ramp-and-soak Omega CN2011 temperature controllers.
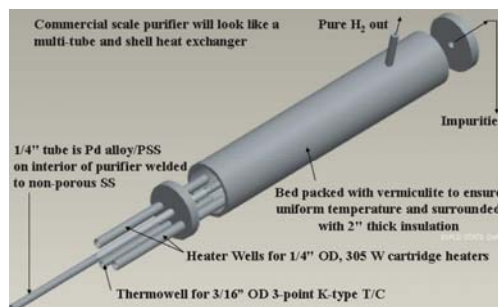
Figure 1   The H_2 purifier

**Figure 2**   Gas handling manifold

3 Results and discussion

3.1 Structural and chemical properties

The aforementioned procedure was established after the first Pd-Ag/PSS sample resulted in a non-uniform sample. More critically, there were cracks in the Pd-Ag layer of the first sample, and the colour looked like that of pure Ag. The non-uniformity and cracking in the Pd-Ag layer were explained by improper control of the electroless bath solution temperature and pH (Shu et al., 1993; Yeung and Cheng, 1999). Moreover, there were heterogeneities on the ends due to handling without gloves after each plating. For this reason, all handling was done on the nonporous ends of the PSS, the bath pH was controlled at 10.4, the bath solution was set to $60 \pm 1°C$, and the supports were anchored to a rotating shaft during deposition to improve uniformity. To verify N_2 impermeability, each sample was leak checked with N_2 at 25°C before welding to a purifier. SEM (Figure 3) and AFM analysis of Pd-coated NPSS showed that the Pd particle size distribution was relatively narrow, with a mean particle size distribution of ~2 μm. On top of the 2 μm particles, were smaller crystals of ~0.2 μm. Despite the apparent pinhole, the film was helium-impermeable.
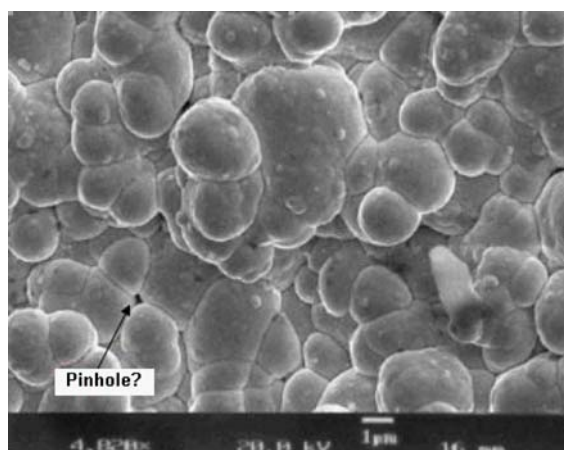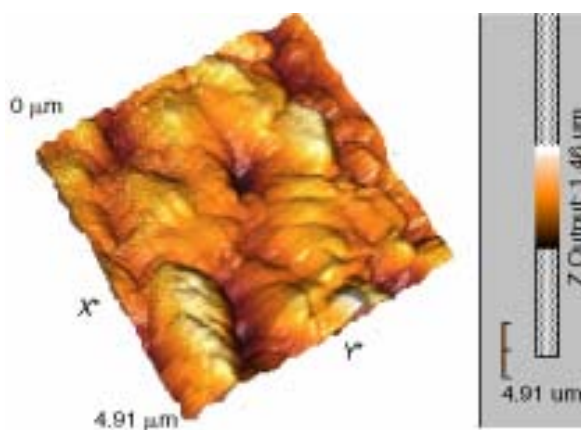

Figure 3   SEM showing the surface topography of a Pd-coated NPSS circular disc after annealing in N_2 for 4 hr at 400°C and for 4 hr at 500°C. Despite the apparent pinhole, the film was leak-tight with respect to helium

Silver deposition is much faster than Pd deposition, because nucleation of Pd is slow; this explains the need for the Sn/Pd activation layer (Shu et al., 1993; Yeung and Cheng, 1999). Figures 4 and 5 show that the Pd-Ag crystals have an average crystallite diameter of ~1 μm. The surface looked like Ag/NPSS. The surface morphology should be controlled by Ag seeding at > 6 at.% Ag, but film composition and morphology are very sensitive to plating bath chemistry (Yeung and Cheng, 1999). The lack of defined particle edges may have indicated incomplete diffusion between subsequent depositions, even under conditions consistent with Ma et al. (2005). EDS analysis on bimetallic samples versus annealing temperature was necessary.
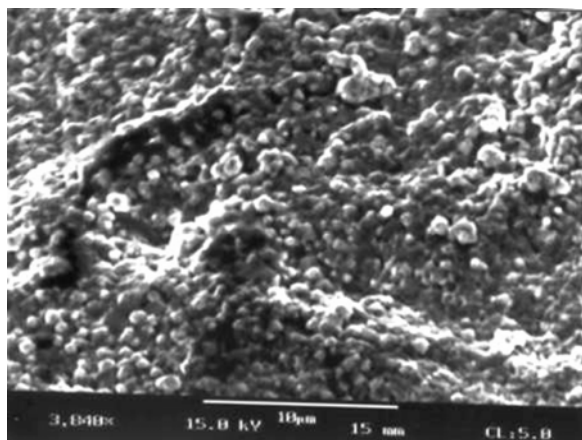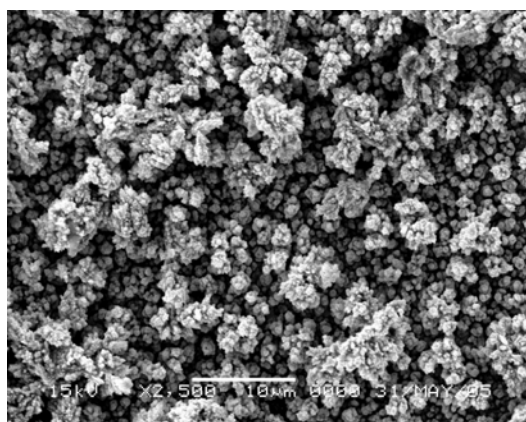
Figure 4   SEM of codeposited Pd-Ag/NPSS after annealing in N_2 for 4 hr at 400°C and
for 4 hr at 500°C

Figure 5   AFM image of codeposited Pd-Ag coated SS circular disc after annealing
in N_2 for 4 hr each at 400°C and at 500°C

The key questions to address via SEM and EDS were whether the films had pinholes,
and in the case of the bimetallic alloy films, whether the Pd and the Ag were properly
alloyed. The latter issue is critical for matching the CTEs to minimise embrittlement.
EDS mapping of some preliminary samples revealed pinholes in some preliminary
samples. Once the aforementioned synthesis controls were applied, this problem was
quickly solved. However, an EDS map (not shown) revealed that 4 hr each at 500°C and
600°C in N_2 was insufficient for proper alloying of samples prepared via coating and
diffusion (Figure 6). PSS-supported Pd-Ag alloys prepared via codeposition and then
annealed at 600°C for 16 hr in N_2 showed that the Ag was uniformly dispersed,
indicating proper alloy formation (Figure 7(a) and (b)). Lower temperatures and times
were insufficient for proper alloy formation, in contradiction with Ma et al. (2005).
EDS revealed the codeposited Pd-Ag/PSS weight percentages of Pd, Ag and Fe, of
78.35, 20.04 and 1.35, respectively. This was close to the desired ratio of 75:25 for Pd
and Ag. A small amount of Fe also diffused from the support into the Pd-Ag membrane.
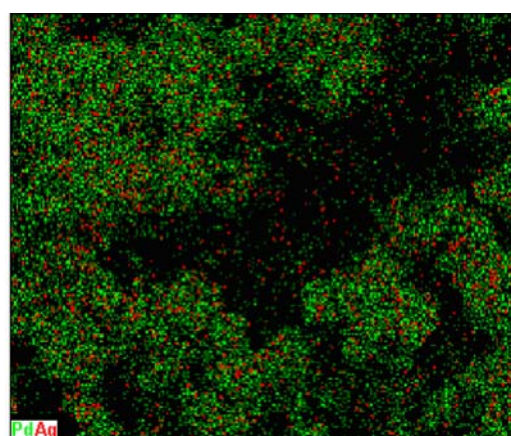
Figure 6   SEM of Pd-Ag alloy on NPSS via the coating and diffusion method. The substrate was annealed for 4 hours each at 500°C & 600°C in N_2
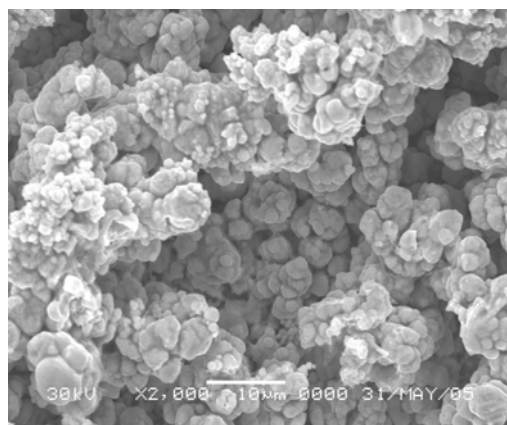

(a)

(b)

Figure 7   (a) SEM of codeposited Pd-Ag/PSS and (b) Codeposited Pd-Ag/PSS EDS map

After realising that at annealing temperatures below 500°C and times less than 10 hr were insufficient to form a proper Pd-Ag alloy, a semi-infinite slab model was used to estimate roughly the temperatures and times required to diffuse Ag uniformly to a desired extent into the Pd layer at a given Pd layer thickness. Based on diffusivity data from Hou and Hughes (2003), the annealing time required for Ag to diffuse uniformly in Pd-Ag layer in subsequent syntheses was calculated. Thin membranes yield both higher fluxes and better alloying (Ma et al., 2003; Tosti et al., 2002). Given that the diffusion times for diffusion distances of 1 μm at 873 K were realistic, all subsequent annealing was done at 873 K for 16 hr to assure that proper alloying was achieved. The benefit of the codeposition method over the coating and diffusion method is the much shorter diffusion distance ($\leq$ 1 μm).

3.2   Permeation results

A N_2 permeance test was conducted at temperature ranges from 573 to 673 K to check for the impermeability of the prepared Pd-Ag purifier membrane. A very modest N_2 permeance of about 0.15–0.25 cm^3/min was detected at trans-membrane pressure difference of 250 kPa, much smaller than the H_2 flow rates (11–21 cm^3/min). A Sievert's Law plot (Figure 8) was also made for the N_2 flux versus the square root of the pressure difference between the retentate (P_r) and permeates side (P_p). This 'law' held true for N_2, implying that N_2 dissociates into two nitrogen atoms from 573 to 673 K. Sievert's Law was derived from a simplification of Fick's Law for the case of dissociative adsorption of hydrogen. Hydrogen, nitrogen, carbon and boron are all interstitial elements that can diffuse through the interstices of certain metals. Like hydrogen, nitrogen is capable of dissociating on certain metals at elevated temperatures. One such metal is iron, for which there is an ample supply in the PSS substrate.
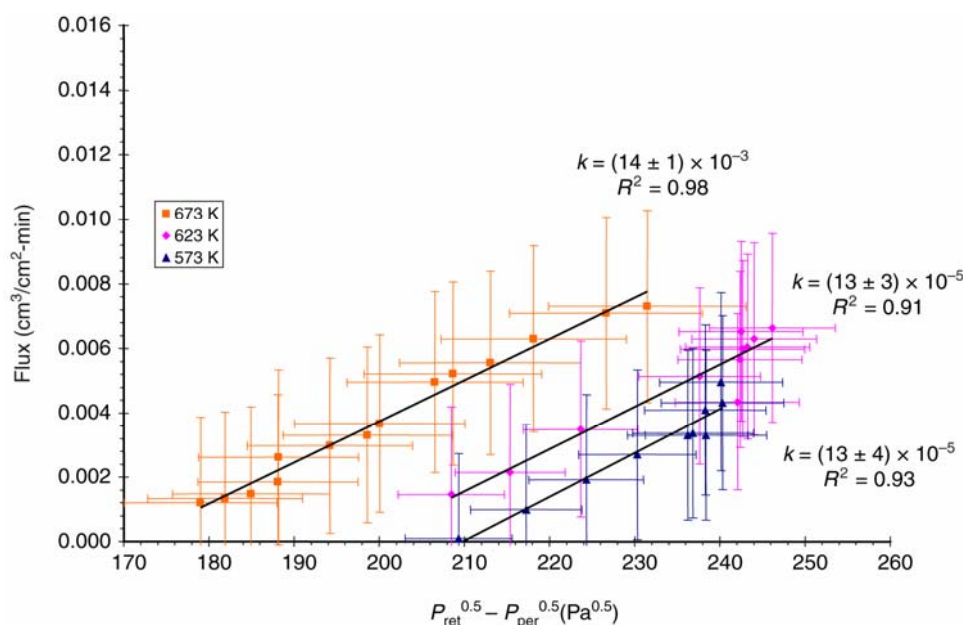
Figure 8   Sievert's Law plot for N_2 flux

Although N_2 flux was found to be temperature dependent, the permeance was found to be independent of temperature. This may indicate pinhole diffusion or grain boundary diffusion, rather than interstitial diffusion, for N_2 permeance. Given the very tiny fluxes involved here and the very low activation energies associated with some bimolecular dissociations, however, it is unclear about the mechanism for nitrogen transport here. The temperature dependence of N_2 solubility, which also factors into permeation rates, is unknown. Once the near impermeability of the prepared Pd-Ag membrane was confirmed with N_2, permeance with H_2 gas across the membrane was confirmed (Figure 9). Helium gas permeances across a series of membranes, including the ones used in Figures 8 and 9, were conducted in response to reviewers' comments, and were below the detection limit.
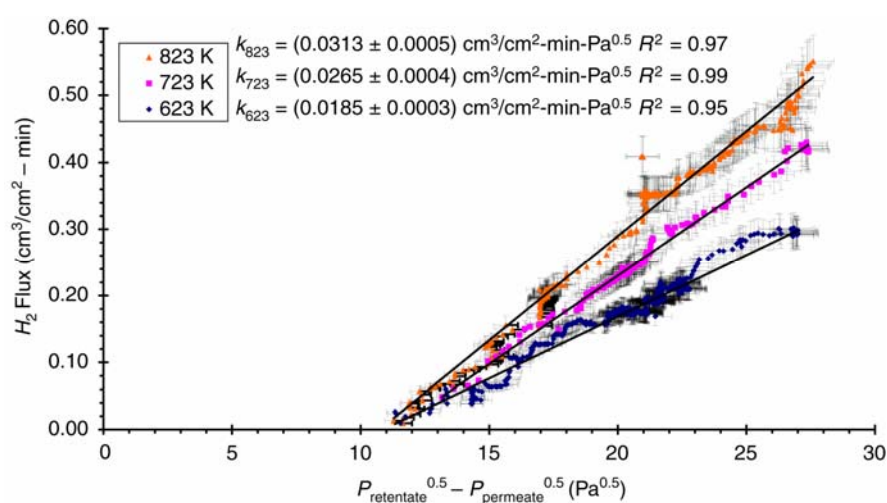
Figure 9   Sievert's Law plot for H_2 permeance

The activation energy of the Pd-Ag membrane was found to be (9 ± 1) kJ/mol with a $R^2 = 0.93$, which was close to the previously reported values for Pd or Pd alloy membranes. A comparison between the derived experimental activation energy value for the Pd-Ag/PSS alloy membrane and those of other researchers is shown in Table 3.

**Table 3**   Activation energies for H_2 permeation

Support	Membrane thickness (μm)	Temp (K)	E_d(kJ/mol)	Reference
Pd/Ag/PSS	48*	623–823	9 ± 1	This work
Pd/PSS	19–28	673–1273	16.38	Mardilovich (1998)
Pd discs	1000	623–1173	13.41	Rothenberger (2003)
Pd/disc	486–762	300–709	11.81	Hurlbert and Konecny (1961)
Pd/Ag/ceramic	0.3	673–993	23	Lin and Jayaraman (1995)
Pd/disc	800–2025	500–900	12.81	Holleck (1970)

*This was the membrane thickness on both sides (inside and outside) of the PSS
 membrane. Pd alloy thickness on one side of the membrane would be 24 microns.
 All the other work reported is for Pd layer only on the outside of the membrane
 substrate.

The H_2 permeability and permeance can also be compared to work done by other researchers in Table 4. Figure 10 compares the H_2 and N_2 fluxes for the Pd-Ag membrane. Preliminary short term hydrogen permeation tests of the Pd-Ag membrane are shown in Figure 11.

Table 4   Comparison of H_2 permeances and permeabilities

T	k (cm^3/cm^2-min-$Pa^{0.5}$)	K (cm^3/cm-min-$Pa^{0.5}$)	*Ref.*
623	$(1.85 \pm 0.03) \times 10^{-2}$	$(8.9 \pm 0.2) \times 10^{-5}$	This work
623	4.33×10^{-2}	9.61×10^{-5}	Tosti et al. (2002)
623	4.15×10^{-2}	9.96×10^{-5}	Hou and Hughes (2003)
673	3.62×10^{-2}	7.78×10^{-5}	Tosti et al. (2002)
673	3.75×10^{-2}	9.00×10^{-5}	Hou and Hughes (2003)
723	$(2.65 \pm 0.04) \times 10^{-2}$	$(12.8 \pm 0.2) \times 10^{-5}$	This work
773	4.30×10^{-2}	8.60×10^{-5}	Ma et al. (2005)
823	$(3.13 \pm 0.05) \times 10^{-2}$	$(15.1 \pm 0.3) \times 10^{-5}$	This work
823	8.70×10^{-3}	2.12×10^{-4}	Uemiya et al. (1991b)
850	1.08×10^{-1}	1.72×10^{-5}	Pan et al. (2003)
1023	3.56×10^{-3}	5.56×10^{-5}	Uemiya et al. (1991b)
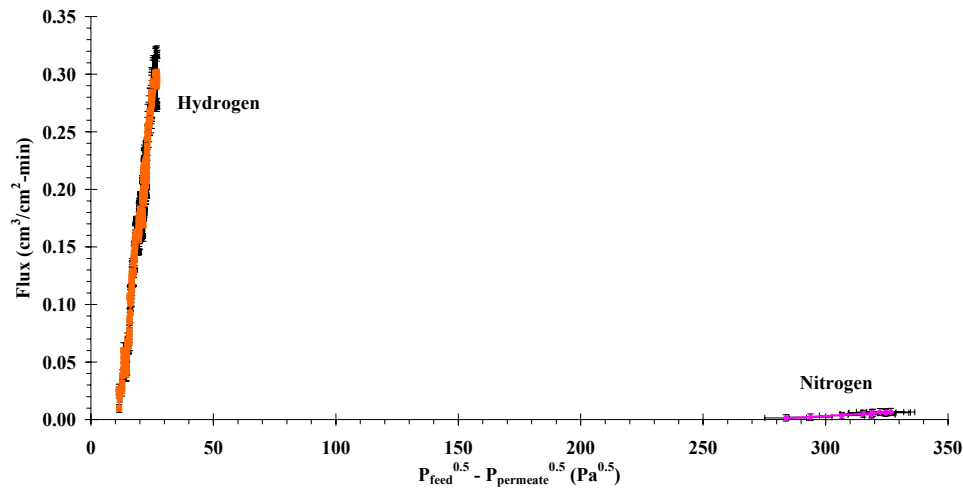
Figure 10 H_2 Flux versus N_2 Flux at 623 K
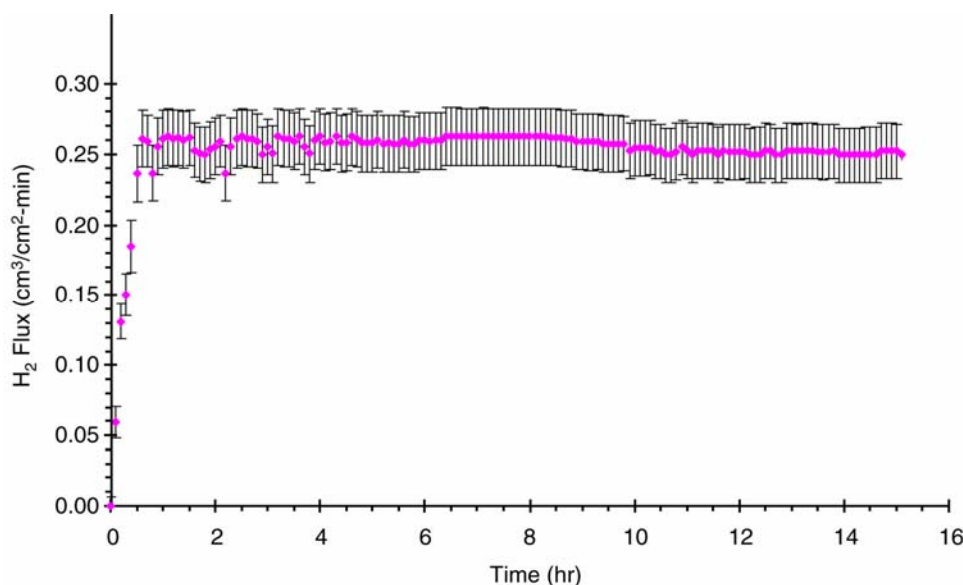
Figure 11 H_2 permeance stability at 623 K

4   Conclusions

1   The proper conditions for codeposition of Pd and Ag from a mixed plating bath were identified and verified: [Metal] = 10 mM, [N_2H_4] = 10 mM, [NH_4OH] = 3M, pH = 10.4 and T = 60°C. Sufficient interdiffusion of the two metals to form a proper alloy requires annealing at 600°C for 16 hr in N_2.

2   SEM-EDS and AFM results concluded that a relatively smooth layer of 79 Pd-21Ag alloy was developed on the PSS substrate with an average Pd-Ag crystal diameter of 0.5 μm with a height variation of about 0.2 μm.

3   EDS revealed that only trace levels of support Fe diffused into the Pd-Ag layers.

4   Very minor N_2 permeation could be detected at temperatures of 573–673 K. The N_2 permeance was found to be constant at 1.3×10^{-4} cm^3/cm^2-min-$Pa^{0.5}$. The magnitude of the N_2 leak was comparable to those reported by Ma et al. (2005). Impermeability of prepared membranes needs to be tested with truly inert gases. The results, however, do not support N_2 diffusing interstitially just like H_2 through Pd-Ag.

5   Membranes composed of thin film of Pd (48 μm) and Pd/Ag deposited on porous stainless steel via electroless plating have been evaluated at temperatures of 623–823 K with H_2 permeability from $(9–15) \times 10^{-5}$ cm^3/cm-min-$Pa^{0.5}$.

6   The activation energy of the Pd-Ag membrane was found to be 9 ± 1 kJ/mol, which was close to the previously reported values for Pd or Pd/Alloy membranes.

7   The reproducibility and short time stability of the H_2 permeation were confirmed.

8   Currently, the flux of hydrogen permeation membranes appears to be limited by the fact that the crystallite diameter of each Pd alloy particle must be large enough to not fall into the pores of the support. In order to increase the H_2 flux substantially, a preparation technique to fabricate multilayer, < 10 nm thick Pd alloy layer will need to be developed. The critical step will involve development of a secondary porosity within the pores of the stainless steel. Currently, we are investigating silica-templated porous carbon/PSS (TPC/PSS) composite supports for high flux Pd alloy hydrogen purification membranes.

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